Additional Priorities: JP 148164/91 240591; JP 150989/91 280591; JP 150980/91 280591; JP 150994/91 280591; JP 150990/91280591, JP 150991/91 280591; JP 150992/91 280591; JP 150981/91 280591; JP 150982/91 280591; JP 150983/91 280591; JP 150984/91280591; JP 150985/91 280591; JP 152249/91 290591; JP 152248/91 290591; JP 149302/91 270591; JP 149297/91 270591; JP 149298/91270591; JP 149300/91 270592;

JP 149299/91 270591; JP 149301/91 270591; JP 150993/91 280591; JP 152250/91 290591; JP 152251/91 290591; JP 149310/91 270591, JP 149306/91 270591; JP 149307/91 270591; JP 149308/91 270591; JP 149309/91 270591; JP 149311/91 270591.

(30) Priority: 1 akaguchi

15.02.91	JP	42212/91
15.02.91	JP	42213/91
28.02.91	JP	55606/91
28.02.91	JP	55605/91
28.02.91	JP	55604/91
28.02.91	JP	55603/91
28.02.91	JP	55602/91
28.02.91	JP	55601/91
28.02.91	JP	55614/91
28.02.91	JP	55613/91
28.02.91	JP	55612/91
28.02.91	JP	55611/91
28.02.91	JP	55610/91
28.02.91	JP	55608/91
28.02.91	JP	55607/91
28.02.91	JP	55609/91
27.03.91	JP	85755/91
24.05.91	JP	148160/91
24.05.91	JP	148161/91
24.05.91	JP	148163/91
	JP	148164/91
	JP	150989/91
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	JP	150981/91
	JP	150982/91
	JP	150983/91
	JP	150984/91
	JP	150985/91
	JP	152249/91
	JP	152248/91
	JP	149302/91
	JP	149297/91
	JP	149298/91
	JP	149300/91
	JP	149299/91

(43) Date of publication of application :
19.08.92 Bulletin 92/34

(84) Designated Contracting States :
AT BE CH DE DK ES FR GB GR IT LI LU NL PT SE

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(54) Etching solution for etching porous silicon, etching method using the etching solution and method of preparing semiconductor member using the etching solution.

(57) A method for preparing a semiconductor member comprises :
forming a substrate having a non-porous silicon monocrystalline layer and a porous silicon layer ;

EP 0 499 488 A2

bonding another substrate having a surface made of an insulating material to the surface of the monocrystalline layer; and
etching to remove the porous silicon layer by immersing in an   tching solution.

BACKGROUND OF THE INVENTION

Fi ld of th Inv ntion

This inv ntion relates to an etching solution for porous silicon, an tching method using th etching s lution and a method of producing a semiconductor memb r using th tching solution. Particularly, this invention relates to a method of producing a semiconductor member which is suitable for separation of dielectric materials or electronic devices, integrated circuits prepared on a monocrystalline semiconductor layer on an insulating material.

Related Background Art

Formation of a monocrystalline Si semiconductor layer on an insulating material has been widely known as the silicon on insulator (SOI) technology, and since a large number of advantages which cannot be reached by bulk Si substrates for preparation of conventional Si integrated circuits are possessed by the device utilizing the SOI structure, so many researches have been done. More specifically, by utilizing the SOI structure, the following advantages can be obtained:

1. Dielectric isolation can be easily done to enable high degree of integration;
2. Radiation hardness is excellent;
3. Stray capacity is reduced to attain high speed;
4. Well formation step can be omitted;
5. Latch-up can be prevented;
6. Fully depleted field effect transistor can be made by thin film formation.

In order to realize the many advantages in device characteristics as mentioned above, studies have been made about the method for forming the SOI structure for these some 10 years. The contents are summarized in, for example, the literature as mentioned below:

Special Issue: "Single-rystal silicon on non-single-crystal insulators"; edited by G. W. Cullen, Journal of Crystal Growth, Volume 63, No. 3, pp. 429 - 590 (1983).

Also, it has been known for a long time to form the SOS (silicon on sapphire) structure by heteroepitaxy of Si on a monocrystalline sapphire substrate by CVD (chemical vapor deposition) method. This was successful to some extent as the most mature SOI technique, but for such reasons as a large amount of crystal defects because of lattice mismatching at the interface between the Si layer and the sapphire substrate, introduction of aluminum from the sapphire substrate into the Si layer, and above all the high cost of the substrate and delay in enlargement of the substrate wafer size, it is obstructed from being widely applied. Relatively in recent years, attempts to realize the SOI structure without use of a sapphire substrate have been done. Such attempts may be broadly classified into the two shown below:

(1) After surface oxidation of an Si monocrystalline substrate, a window is formed to have the Si substrate partially exposed, and epitaxial growth is proceeded in the lateral direction with that exposed portion as the seed to form an Si monocrystalline layer on SiO$_2$. (In this case, deposition of Si layer on SiO$_2$ is accompanied).

(2) By use of an Si monocrystalline substrate itself as an active layer, SiO$_2$ is formed therebeneath. (This method is accompanied wit no deposition of Si layer).

As the means for realizing the above (1), there have been known the method in which a monocrystalline Si layer is formed directly to lateral epitaxial growth by CVD, the method in which amorphous Si is deposited and subjected to solid phase lateral epitaxial growth by heat treatment, the method in which an amorphous or polycrystalline Si layer is irradiated convergently with an energy beam such as electron beam, laser beam, etc. and a monocrystalline layer is grown on SiO$_2$ by melting and recrystallization, and the method in which a melting region is scanned in a zone fashion by a rod-shaped heater (Zone melting recrystallization). These methods have both advantages and disadvantages, they still have many problems with respect to controllability, productivity, uniformity and quality, and none of them have been industrially applied yet up to date. For example, the CVD method requires sacrifice-oxidation in flat thin film formation, while the crystallinity is poor in the solid phase growth method. On the other hand, in the beam annealing method, problems are involved in controllability such as treatment time by converged beam scanning, the manner of overlapping of beams, focus adjustment, etc. Among these, the Zone Melting Recrystallization method is the most mature, and a relatively larger scale integrated circuit has been trially made, but still a large number of crystal defects such as point defects, line defects, plane defects (sub-boundary), etc. remain, and no device driven by minority carriers has been prepared.

Concerning the m thod using no Si substrat as th seed for epitaxial growth which is th ab v method

3

(2), for exampl , the following method may b included.

1. An oxid film is formed on an Si monocrystallin substrate with V-grooves as anis tropically tched on th surface, a polycrystallin Si lay r is d posited on the oxid film thick to th extent as th Si substrate, and th reafter by polishing from th back surface of the Si substrate, Si monocrystallin regions di lectrically separated by surrounding with th V-grooves on th thick polycrystalline Si lay r are formed. In this method, although crystallinity is good, there are problems with respect to controllability and productivity in the step of depositing the polycrystalline Si thick as some hundred microns and the step in which the monocrystalline Si substrate is polished from the back surface to leave only the Si active layer as separated.

2. This is the method called SIMOX (Separation by Ion-implanted oxygen) in which an SiO$_2$ layer is formed by Ion implantation of oxygen into an Si monocrystalline substrate, which is one of the most mature methods because of good matching with the SI-IC (Integrated Circuit) process. However, for formation of the SiO$_2$ layer, 10^{18} ions/cm^2 or more of oxygen ions are required to be implanted, and the implantation time is very long to be not high in productivity, and also the wafer cost is high. Further, many crystal defects remain, and from an industrial point of view, no sufficient level of quality capable of preparing a device driven by minority carriers have been attained.

3. This is the method to form an SOI structure by dielectric isolation according to oxidation of porous Si. This is a method in which an N-type Si layer is formed on the surface of a P-type Si monocrystalline substrate in shape of islands by way of proton ion implantation (Imai et al., J. Crystal Growth, Vol. 63, 547 (1983)), or by epitaxial growth and patterning; only the P-type Si substrate is made porous by anodization in HF solution so as to surround the Si islands from the surface; and then the N-type Si islands are dielectrically isolated by accelerated oxidation. In this method, the separated Si region is determined before the device steps, whereby there is the problem that the degree of freedom in drive and circuit design may be limited in some cases.

A light-transmissive substrate is important for forming a contact sensor serving as a light-receiving device and a projection-type liquid crystal image display. A high-quality driving device is required for further increasing the density, resolution and definition of the pixels (picture element) of such a sensor or display. It is consequently necessary to produce a device to be provided on a light-transmissive substrate by using a monocrystalline layer having excellent crystallinity.

However, if an Si layer is deposited on a light-transmissive substrate such as glass substrate, etc., the Si layer is generally an amorphous layer or, at best, a polycrystalline layer because the Si layer reflects the disorder of the crystal structure of the substrate, and no high-quality device can thus be formed by using the Si layer. This is because the substrate has an amorphous crystal structure, and thus a monocrystalline layer of high quality cannot be easily obtained by simply depositing the Si layer. It is therefore difficult to produce a driving device having properties sufficient for the present demands or future demands because the crystal structure of an amorphous Si or polycrystalline Si has many defects.

Further, any one of the methods using an Si monocrystalline substrate is unsuitable for obtaining a good monocrystalline film on a light-transmissive substrate.

Takao Yonehara, one of the inventors, previously proposed a method of forming a semiconductor substrate which is capable of solving the above problems in Japanese Patent Application No. 2-206548.

The method of forming a semiconductor substrate disclosed in Patent Application No. 2-206548 comprises forming a substrate having a non-porous semiconductor monocrystalline layer and a porous semiconductor layer, bonding another substrate having an insulating material surface to the surface of the monocrystalline layer, and removing the porous semiconductor layer by etching.
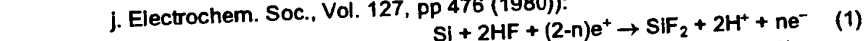
This invention has been achieved for improving the invention disclosed in Patent Application No. 2-206548 previously proposed.
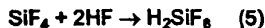
The method of forming a semiconductor substrate disclosed in Patent Application No. 2-206548 comprises the step of removing porous Si by selective etching.

Porous Si is described below.

Porous Si was discovered in the course of research on electrolytic polishing of a semiconductor which was conducted by Uhlir et al, in 1956 (A. Uhlir, Bell Syst. Tech. J., Vol. 35, pp 333 (1956)).

Unagami et al. investigated dissolving reaction of Si during anodization and reported that the anodic reaction of Si in a HF solution requires positive holes, and that the reaction is expressed as follows (T. Unagami, J. Electrochem. Soc., Vol. 127, pp 476 (1980)):

$$Si + 2HF + (2-n)e^+ \rightarrow SiF_2 + 2H^+ + ne^- \quad (1)$$
$$SiF_2 + 2HF \rightarrow SiF_4 + H_2 \quad (2)$$
$$SiF_4 + 2HF \rightarrow H_2SiF_6 \quad (3)$$

Or

$$Si + 4HF + (4-\lambda)^+ \rightarrow SiF_4 + 4H^+ + \lambda e^- \quad (4)$$

$$SiF_4 + 2HF \rightarrow H_2SiF_6 \quad (5)$$

wherein $+$ and $-$ respectiv ly denote a positive hole and an lectron, and n and λ each d notes th number of positive hol s required for dissolving one silicon atom. Porous Si can be formed when the condition, n > 2 or λ > 4, is satisfied.

It is therefore found that positive holes are required for forming porous Si, and that P-type Si can be more easily made porous than N-type Si. However, it is also known that N-type Si can be made porous if holes are implanted thereto (R. P. Holmstrom and J. Y. Chi, Appl. Phys. Lett., Vol. 42, 386 (1983)).

The density of the porous Si layer can be changed to the range of 1.1 to 0.6 g/cm³ by changing the concentration of the HF solution from 50 to 20%, as compared with the density of 2.33 g/cm³ of monocrystalline Si. The porous Si layer has pores having an average size of about 600 Å which was measured by observation by a transmission electron microscope. Although the porous Si layer has a density which is half or less than that of monocrystalline Si, monocrystallinity is maintained, and a monocrystalline Si layer can be formed on the porous layer by epitaxial growth.

Although the volume of an Si monocrystal is generally increased by 2.2 times by oxidation, the increase in volume can be suppressed by controlling the density of the porous Si so that the occurrence of curvature of a substrate or the occurrence of a crack in a monocrystalline layer remained on the surface can be avoided during the oxidation process. The volume ratio R of monocrystalline Si to porous Si after oxidation can be expressed as follows:

$$R = 2.2 \times (A/2.33) \quad (6)$$

wherein A denotes the density of porous Si. If R = 1, i.e., there is no increase in volume after oxidation, A = 1.06 (g/cm³). Namely, if the density of the porous Si layer is 1.06, an increase in volume, which is caused by oxidation, can be suppressed.

It can be said that at present, porous Si is subjected as such directly to subsequent steps (epitaxial growth and oxidation) after producting it, and the porous Si itself is not processed. This is because the porous Si cannot be easily processed or removed with good controllability. Namely, it has been not reported yet that porous Si is etched with good controllability.

In addition, P generally shown by the following equation is referred as porosity:

$$P = (2.33 - A)/2.33 \quad (7)$$

When the value of porosity is adjusted to 30 to 55% during anodization, the properties of oxidized porous Si can be equalized to those of a monocrystalline Si oxide film. The porosity is expressed as follows:

$$P = (m1 - m2)/(m1 - m3) \quad (8)$$

or

$$P = (m1 - m2)/\rho At \quad (9)$$

wherein

m1: total weight before anodization
m2: total weight after anodization
m3: total weight after removal of porous Si
ρ: density of monocrystalline Si
A: area of porous region
t: thickness of porous Si

However, the area of the porous region cannot be accurately calculated in many cases. In this case, although the equation (8) is effective, the porous Si must be etched for measuring the value of m3.

In addition, during epitaxial growth on the porous Si, the porous Si is capable of relieving distortion produced during heteroepitaxial growth and suppressing the occurrence of defects. However, in this case, since it is clear that the porosity is a very important parameter, measurement of the porosity is necessary and indispensable.

Known methods of etching porous Si are the following methods (1) and (2):

(1) The method of etching porous Si with an aqueous NaOH solution (G. Bonchil, R. Herino, K. Barla, and J. C. Pfister, J. Electrochem. Soc., Vol. 130, No. 7, 1611 (1983)).

(2) The method of etching porous Si with an etching solution which is capable of etching non-porous Si.

In the above method (2), a fluoronitric acid-type etching solution is generally used, and etching of Si proceeds as follows:

$$Si + 2O \rightarrow SiO_2 \quad (10)$$
$$SiO_2 + 4HF \rightarrow SiF_4 + H_2O \quad (11)$$
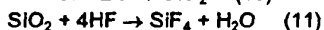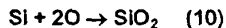
As shown by the above reaction formulas, Si is oxidized to SiO₂, and the SiO₂ produced is etched with hydrofluoric acid.

Examples of etching solutions for non-porous Si include the above fluoronitric acid-type etching solution as well as ethylenediamine-type, KOH-type and hydrazine-type etching solutions and the like.

In this invention, it is necessary in selective tching of porous Si to select an etching solution which is cap-

able of etching porous Si, other than th above tching solutions for non-porous Si. The porous Si is generally selectively etch d by the above method (1) which us s an aqueous NaOH solution as an tching solution.

As d scrib d abov , both porous and non-porous Si are etched with th fluoronitric acid-typ etching s l-ution.

On the other hand, in the conventional m thod of selectiv ly tching porous Si with an aqueous NaOH ol-ution, Na ions are inevitably adsorbed on the etched surface. Since the Na ions cause impurity contamination, are movable and have adverse effects such as the formation of a interfacial states, the ions must not be intro-duced into the semiconductor process.

SUMMARY OF THE INVENTION

An object of this invention is to provide an etching solution which efficiently, uniformly, selectively and chemically etches porous Si without affecting the semiconductor process and etching non-porous Si.

Another object of this invention is to provide a method of preparing a semiconductor member using an etch-ing solution for uniformly and selectively etching porous Si.

BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1A and 1B are schematic views explaining an etching step using an etching solution of this invention;

Figs. 2A and 2B are schematic views explaining an etching step using an etching solution of this invention;

Figs. 3A to 3C are schematic views explaining an etching step using an etching solution of this invention;

Figs. 4A to 4C are schematic views explaining an etching step using an etching solution of this invention;

Figs. 5A to 5D are schematic views explaining an etching step using an etching solution of this invention;

Figs. 6A to 6H are graphs showing the etching properties of porous and non-porous Si when etching sol-utions of this invention are respectively used;

Figs. 7A to 7H are graphs showing the relations between the etched thickness (etching depth) of porous Si and etching time when etching solutions of this invention are respectively used;

Figs. 8A to 8C are schematic views explaining a process for preparing a semiconductor member of this invention;

Figs. 9A to 9D are schematic views explaining a process for preparing a semiconductor member of this invention;

Figs. 10A to 10C are schematic views explaining a process for preparing a semiconductor member of this invention;

Figs. 11A to 11D are schematic views explaining a process for preparing a semiconductor member of this invention;

Figs. 12A to 12C are schematic views explaining a process for preparing a semiconductor member of this invention;

Figs. 13A to 13C are schematic views explaining a process for preparing a semiconductor member of this invention; and

Figs. 14A to 14D are schematic views explaining a process for preparing a semiconductor member of this invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

According to one aspect of this invention, this invention provides a chemical etching solution for etching porous silicon.

A first embodiment of the chemical etching solution of this invention is hydrofluoric acid.

A second embodiment of the chemical etching solution is a mixture containing hydrofluoric acid and an alcohol.

A third embodiment of the chemical etching solution is a mixture containing hydrofluoric acid and hydrogen peroxide.

A fourth embodiment of the chemical etching solution is a mixture containing hydrofluoric acid, an alcohol and hydrogen peroxide.

A fifth embodiment of the chemical etching solution is buffered hydrofluoric acid.

A sixth embodiment of the chemical etching solution is a mixture containing buffered hydrofluoric acid and an alcohol.

A seventh embodiment of the chemical etching solution is a mixture containing buffered hydrofluoric acid and hydrogen peroxid .

A eighth mbodiment of th chemical etching solution is a mixture of buffered hydrofluoric acid, an alcohol and hydrogen peroxide.

Th tching method of this invention comprises selectively tching porous silicon using th tching soluti n of this inv ntion.

According to anoth r asp ct of this inv ntion, this invention provides a m thod of preparing a semiconductor m mb r.

A first embodiment of the method of preparing a semiconductor member of this invention comprises forming a substrate having a non-porous monocrystalline silicon layer and a porous silicon layer, bonding another substrate having a surface made of insulating material to the surface of the monocrystalline layer, and etching the porous silicon layer by immersing it in hydrofluoric acid.

A second embodiment of the method of preparing a semiconductor member of this invention uses each of the second to eighth forms of the etching solution of this invention in place of hydrofluoric acid used as an etching solution in the first form of the method of preparing a semiconductor member of this invention.

A third embodiment of the method of:preparing a semiconductor member of this invention comprises the steps of making a silicon substrate porous, forming a non-porous monocrystalline silicon layer on the silicon substrate made porous, bonding a light-transmissive glass substrate to the surface of the non-porous monocrystalline silicon layer, and selectively etching porous silicon so as to remove porous silicon by chemical etching using an etching solution of this invention by immersing the silicon substrate made porous therein.

A fourth embodiment of the method of preparing a semiconductor member of this invention comprises the steps of making a silicon substrate porous, forming a non-porous monocrystalline silicon layer on the silicon substrate made porous, bonding another silicon substrate having an insulating layer on the surface thereof to the surface of the non-porous monocrystalline silicon layer, and selectively etching porous silicon so as to remove porous silicon by chemical etching using an etching solution of this invention by immersing the silicon substrate made porous therein.

A fifth embodiment of the method of preparing a semiconductor member of this invention comprises the steps of making a silicon substrate porous, forming a non-porous monocrystalline silicon layer on the silicon substrate made porous, forming an oxide layer on the surface of the non-porous monocrystalline silicon layer, bonding a light-transmissive substrate to the surface of the oxide layer and selectively etching the silicon substrate made porous to remove it by chemical etching using an etching solution of this invention by immersing the silicon substrate made porous therein.

A sixth embodiment of the method of preparing a semiconductor member of this invention comprises the steps of making a silicon substrate porous, forming a non-porous monocrystalline silicon layer on the silicon substrate made porous, forming an oxide layer on the surface of the non-porous monocrystalline silicon layer, bonding another silicon substrate having an insulating layer on the surface thereof to the oxide layer formed on the non-porous monocrystalline silicon layer, and selectively etching the silicon substrate made porous to remove it by chemical etching using an etching solution of this invention by immersing the silicon substrate made porous therein.

In each of the above embodiments according to the method of preparing a semiconductor member of the present invention, the etching step may be carried out with coating the surfaces other than the surface of the silicon layer made porous with a protecting material before etching.

The etching solution for porous Si of this invention is capable of uniformly and efficiently etching porous Si without the danger of contaminating the semiconductor process.

The etching method of this invention can be applied to usual semiconductor processes and is capable of selectively etching, with high accuracy, the porous Si provided on the same substrate provided non-porous Si to remove the porous Si because a chemical etching solution which does not etch non-porous Si is used.

The method of preparing a semiconductor member of this invention is excellent in productivity, uniformity, controllability and economy for forming a crystalline Si layer having excellent crystallinity equal to that of a monocrystalline wafer on insulating substrates such as light-transmissive insulating substrates represented by a glass substrate.

The method of preparing a semiconductor member of this invention is capable of realizing the advantages of conventional SOI devices and can be applied to various fields.

The method of preparing a semiconductor member of this invention can also be used in place of the expensive SOS or SIMOX used for producing a large-scale integrated circuit having the SOI structure.

In addition, the method of preparing a semiconductor member of this invention comprises the steps of chemically removing the lower portion of a monocrystalline Si substrate of high quality used as a starting material, with leaving only a monocrystalline layer on the surface thereof, and bonding the substrate to an insulating layer, and thus enables many treatments to be performed for a short time and has excellent productivity and economy.

7

Further, the method of preparing a semiconductor member of this inventi n can use a ch mical tching solution which has a bad eff ct on th s miconductor process in tching f porou Si and xhibits an etching selection ratio of a fiv digits value or more of porous Si to non-porous Si and xcellent controllability and productivity.

I. A description will now be given of th etching solution in accordance with th present inv ntion.

I-(1)

A description will be made first as to the case where hydrofluoric acid is used as the electroless wet chemical etching solution for porous Si, with specific reference to Fig. 7A.

Fig. 7A shows the etching time dependency of etched thickness of porous Si when the latter is etched by being immersed in hydrofluoric acid. The porous Si was formed by anodizing a monocrystalline Si. The conditions of anodization are shown below. It is to be noted, however, that the starting material for producing porous Si by anodization is not limited to monocrystalline Si and Si of other crystalline structure may be used as the starting material.

Voltage applied:	2.6 (V)
Current density:	30 (mA·cm^{-2})
Anodizing solution:	HF:H$_2$O:C$_2$H$_5$OH = 1 : 1 : 1
Time:	2.4 hours
Thickness of porous Si:	300 (µm)
Porosity:	56 (%)

Test pieces of the porous Si thus prepared were immersed in 49 % hydrofluoric acid solution (white circles) and 20 % hydrofluoric acid solution (black circles) both at the room temperature, and the solutions were agitated. The reduction in the thickness of these test pieces of the porous Si were then measured. A large etching rate was observed: namely, 90 µm in 40 minutes in case of the 49 % hydro hydro acid solution and 72 µm in 40 minutes in case of the 20 % hydrofluoric acid solution. After elapse of 80 minutes, the porous Si test pieces were etched by 205 µm with a high degree of surface state in case of the 49 % hydrofluoric acid solution, whereas, in case of the 20 % hydrofluoric acid solution, the etching depth was 164 µm after elapse of 80 minutes.

The etching rate has dependencies on the concentration of the etching solution and the temperature. The etching solution concentration and temperature are suitably determined in practical ranges. Although solution concentration of 49 % and 20 % and the room temperature are mentioned above, these are only illustrative and are not intended for limiting purpose. Preferably, the concentration of the hydrofluoric acid ranges between 5 % and 95 % and the temperature of the solution is set to a level which is ordinarily adopted in this field of technology.

The etched test pieces of porous Si were then rinsed with water and the surfaces after the rinsing were examined by microanalysis using secondary ions but no impurity was detected.

A description will now be given with specific reference to Fig. 6A of the etching characteristics of porous Si and non-porous Si when hydrofluoric acid is used as the etching solution, followed by a description of an example of etching of a non-porous Si substrate whose one side surface is completely porous Si, taken in conjunction with Figs. 1A and 1B.

Fig. 6A is a graph showing the time dependency of etching depth of porous Si and monocrystalline Si as observed when they are immersed in hydrofluoric acid solution. Porous Si was formed by anodizing monocrystalline Si under the same conditions as those mentioned above. In this case also, the use of monocrystalline Si as the starting material for anodization is only illustrative and Si of other crystalline structures may be used as the starting material.

Test pieces of the porous Si thus prepared were immersed in 49 % hydrofluoric acid solution (white circles) at the room temperature, and the solutions were agitated. The reduction in the thickness of these test pieces of porous Si were then measured. A large etching rate was observed: namely, 90 µm in 40 minutes in case of the 49 % hydrofluoric acid solution and, after elapse of 80 minutes, the porous Si test pieces were etched by 205 µm with a high degree of surface state. The etching rate has dependencies on the concentration of the etching solution and the temperature. The etching solution concentration and temperature are suitably determined in practical ranges. Although solution density of 49 % and the room temperature are mentioned above, these are only illustrative and are not intended for limiting purpose. Preferably, the concentration of the hydroflu ric acid ranges between 5 % and 95 % and the temperature of the solution is set to a level which is ordinarily adopt d in this field of t chn logy.

A test piece of a non-porous Si of 500 µm thick was immersed in a 49 % solution of hydrofluoric acid (black

circles), followed by an agitation of the solution. The reduction in the thickn ss was th n measured. In this case, th test pi ce of non-porous Si was etched only by 100 Angstrom r less even after elaps of 120 minutes. Th tching rate showed almost no d pendency on s lution concentration and t mperature.

Both th porous and non-porous Si test pieces aft r th etching were rinsed with water and th surface states of thes test pi ces wer xamin d by microanalysis with s condary i ns but no impurity was detected.

As shown in Fig. 1A, a monocrystallin Si substrate 22 was anodized nly at its ne sid s as to have a porous Si structure only at its one side as denoted by 21. Then, the substrate having the porous Si/monocrys-talline Si structure was immersed in a hydrofluoric acid. As a consequence, only the porous Si portion was removed by the etching while the monocrystalline Si substrate 22 alone remained unetched. It is thus possible to selectively etch porous Si by using monocrystalline Si as the etch stopper.

A description will now be given of a case where both porous Si portion and monocrystalline Si portion are provided on one side of the substrate.

As shown in Fig. 2A, a portion of one side of a monocrystalline Si substrate 32 was anodized to become porous Si structure 31. Since the current and voltage necessary for the anodization vary depending on the car-rier concentration, it is possible to selectively form porous Si structure by locally varying the carrier concen-tration in the monocrysta11ine Si surface layer through implantation of proton or impurities. The substrate having the porous Si/monocrystalline Si structure was then immersed in hydrofluoric acid. As a result, only the porous Si portion was removed while the monocrystalline Si substrate 32 remained unetched. It is thus possible to selectively etch porous Si.

A description will be made as to the case where a porous Si structure and a polycrystalline structure are formed in layers on one side of the substrate.

As shown in Fig. 3A, a polycrystalline Si layer 41 was formed by deposition on a single-crystalline Si sub-strate 42, and the surface layer of this polycrystalline Si was changed into a porous Si layer 43 by anodization, as shown in Fig. 3B. The substrate having the porous Si/polycrystalline Si/monocrystalline Si structure was immersed in a solution of hydrofluoric acid, whereby the porous Si structure alone was removed by etching while the monocrystalline Si substrate 42 and the polycrystalline Si layer 41 remained unetched. It was thus possible to selectively etch the porous Si by using polycrystalline Si as the etching stopper.

A description will now be given of a case where porous Si portion is formed in the surface of a polycrystalline Si layer which is formed on one side of the substrate.

As shown in Fig. 4A, a polycrystalline Si layer 51 was formed by deposition in a monocrystalline Si substrate 52 and a portion of this polycrystalline Si layer was changed into porous Si layer 53 by anodization. Then, the substrate having the porous Si/polycrystalline Si/monocrystalline Si structure was immersed in a solution of hydrofluoric acid, so that the porous Si alone was removed while the monocrystalline Si substrate 52 and the polycrystalline Si layer 51 remained unetched. It was thus possible to selectively etch the porous Si

I-(2)

A description will now be given of the case where a mixture of hydrofluoric acid and an alcohol is used as the electroless wet chemical etching solution for porous Si, with reference to Fig. 7B.

Fig. 7B shows the time dependency of etching thickness of porous Si as observed when the porous Si is immersed in a mixture liquid of hydrofluoric acid and ethyl alcohol without agitation of the liquid. The porous Si was formed by anodizing monocrystalline Si under the conditions shown below. The use of the monocrys-talline Si as the starting material for forming the porous Si structure through anodization is only illustrative and Si of other crystalline structures can be used as the starting material.

Voltage applied: 2.6 (V)
Current density: 30 (mA·cm^{-2})
Anodizing solution: HF:H$_2$O:C$_2$H$_5$OH = 1 : 1 : 1
Time: 2.4 (hours)
Thickness of porous Si: 300 (µm)
Porosity: 56 (%)

Test pieces of the porous Si prepared as described above were immersed, without agitation, in a mixture solution of 49 % hydrofluoric acid and ethyl alcohol (10 : 1) (white circles) and in a mixture solution of 20 % hydrofluoric acid and ethyl alcohol (10 : 1) (black circles). The reductions in the thicknesses of the porous Si test pieces were then measured. Large rates of etching of the porous Si were observed: namely, in the case of the mixture solution of 49 % hydrofluoric acid and ethyl alcohol (10 : 1), the porous Si was etched by 85 µm and, in case of the mixture solution of 20 % hydrofluoric acid and ethyl alcohol (10 : 1), the porous Si was etched by 68 µm, in about 40 minutes. After elaps of 80 minutes, th p rous Si was etch d by a thickness as large as 195 µm in th cas of the mixtur solution of 49 % hydroflu ric acid and ethyl alcoh l (10 : 1) and 156 µm

even in th case of th mixture solution of 20 % hydrofluoric acid and ethyl alcoh l (10 : 1), with high degrees of states of the tched surfaces.

The tching rate has depend ncies on the concentration of the hydrofluoric acid solution, as w ll as n the temp rature. Th addition of alcohol s rves to remove bubbles of reaction product gases g nerated as a result of th etching without delay from th surface b ing etched, without necessitating agitation, thus nsuring a high efficiency and uniformity of th etching.

The solution concentration and the temperature are determined such that a practical etching speed is obtained in preparation process and the effect of addition of alcohol is appreciable. Although the mixture solutions of 49 % hydrofluoric acid and ethyl alcohol (10 : 1) and 20 % hydrofluoric acid and ethyl alcohol (10 : 1), as well as the room temperature as the solution temperature, are mentioned, these solution densities and temperature are only illustrative and are not intended to restrict the scope of the invention. The HF concentration with respect to the etching solution preferably ranges between 1 and 95 %, more preferably between 5 and 90 % and most preferably between 5 and 80 %. The concentration of alcohol with respect to the etching solution is preferably 80 % or less, more preferably 60 % or less and most preferably 40 % or less, and is determined so as to provide an appreciable effect of addition of the alcohol. The temperature is selected to range preferably 0 to 100°C, more preferably 5 to 80°C and most preferably 5 to 60°C.

Although ethyl alcohol has been mentioned specifically, the invention does not exclude the use of other alcohol such as isopropyl alcohol which does not cause any inconvenience in the production process and which can provide an appreciable effect of addition of such alcohol.

The porous Si after the etching was rinsed with water and the rinsed surface was examined by micro-analysis by using secondary ions but no impurity was detected.

A description will now be given of the etching characteristic of porous Si and non-porous Si when they are etched by a mixture solution of hydrofluoric acid and ethyl alcohol, with specific reference to Fig. 6B.

Fig. 6B shows time dependencies of etched thicknesses of porous Si and monocrystalline Si as observed when the porous Si and the monocrystalline Si are immersed in a mixture solution of hydrofluoric acid and ethyl alcohol without agitation. The porous Si was formed by anodization of monocrystalline Si conducted under the same conditions as those shown before. The use of monocrystalline Si as the starting material for forming porous Si through anodization is only illustrative and Si of other crystalline structures can be used as the starting material.

A test piece of porous Si prepared as described above was immersed, without agitation, in a mixture solution of 49 % hydrofluoric acid and ethyl alcohol(10 : 1) (while circles), and reduction in the thickness of the porous Si was measured. The porous Si was rapidly etched: namely, by a thickness of 85 μm in 40 minutes and 195 μm in 80 minutes, with high degrees of surface quality and uniformity.

The etching rate depends on the concentration and the temperature of the hydrofluoric acid solution.

The addition of alcohol serves to remove bubbles of reaction product gases generated as a result of the etching without delay from the surface being etched, without necessitating agitation, thus ensuring a high efficiency and uniformity of the etching.

A test piece of a non-porous Si of 500 μm thick was immersed in a mixture solution of 49 % hydrofluoric acid and ethyl alcohol (10 : 1) (black circles), without agitation of the solution. The reduction in the thickness was then measured. In this case, the test piece of non-porous Si was etched only by 100 Angstrom or less even after elapse of 120 minutes. The etching rate showed almost no dependency on the solution concentration and temperature.

Both the porous and non-porous Si test pieces after the etching were rinsed with water and the surface states of these test pieces were examined by microanalysis with secondary ions but no impurity was detected.

Naturally, various etching methods explained in connection with l by making reference to Figs. 1A and 1B, Figs. 2A and 2B, Figs. 3A to 3C and Figs. 4A to 4C can be realized also in the case where the mixture solution of hydrofluoric acid and an alcohol is used as the etchant for porous Si.

l-(3)

A description will now be given of the case where a mixture of hydrofluoric acid and aqueous hydrogen peroxide (hereinafter also referred to as "hydrogen peroxide") is used as the electroless wet chemical etching solution for porous Si, with reference to Fig. 7C.

Fig. 7C shows the time dependency of etched thickness of porous Si as observed when the porous Si is immersed in a mixture liquid of hydrofluoric acid and hydrogen peroxide under agitation of the liquid. The porous Si was formed by anodizing monocrystalline Si under the conditions shown below. The use of the monocrys-tallin Si as the starting material for forming th porous Si structure through anodization is nly illustrative and Si of other crystalline structures can be used as the starting mat rial.

Voltage applied:	2.6 (V)
Current density:	30 (mA·cm⁻²)
Anodizing solution:	$HF:H_2O:C_2H_5OH = 1 : 1 : 1$
Time:	2.4 (hours)
Thickn ss of porous Si:	300 (μm)
Porosity:	56 (%)

Test pieces of the porous Si prepared as described above were immersed, without agitation, in a mixture solution of 49 % hydrofluoric acid and hydrogen peroxide (1 : 5) (white circles) and in a mixture solution of 49 % hydrofluoric acid and hydrogen peroxide (1 : 1) (black circles). The reductions in the thicknesses of the porous Si test pieces were then measured. Large rates of etching of the porous Si were observed: namely, in the case of the 1 : 5 solution, the porous Si was etched by 112 μm and, in case of the 1 : 1 solution, the porous Si was etched by 135 μm, in about 40 minutes. After elapse of 80 minutes, the porous Si was etched by a thickness as large as 256 μm in the case of the 1 : 5 solution and 307 μm in the case of the 1 : 1 solution, with high degrees of states of the etched surfaces. The concentration of hydrogen peroxide was 30 % in this case but the hydrogen peroxide concentration may be determined in a range which provides an appreciable effect of addition of hydrogen peroxide and which does not cause any practical problem in the production process.

The etching rate has dependencies on the density of the hydrofluoric acid solution, as well as on the temperature of the same. The addition of alcohol serves to accelerate oxidation of silicon, thus enhancing the reaction speed as compared to the case where hydrogen peroxide is not used. It is also possible to control the reaction speed by suitably selecting the content of hydrogen peroxide.

The solution concentration and the solution temperature are determined such that a practical etching speed is obtained in preparation process and the effect of hydrofluoric acid and hydrogen peroxide is appreciable. Although the mixture solutions of 49 % hydrofluoric acid and hydrogen peroxide (1 : 5) and 49 % hydrofluoric acid and hydrogen peroxide (1 : 1), as well as the room temperature as the solution temperature, are mentioned, these solution concentrations and temperature are only illustrative and are not intended to restrict the scope of the invention.

The HF concentration with respect to the etching solution preferably ranges between 1 and 95 %, more preferably between 5 and 90 % and most preferably between 5 and 80 %. The concentration of H_2O_2 with respect to the etching solution is preferably selected to range between 1 and 95 %, more preferably between 5 and 90% and most preferably between 10 and 80%, and is determined so as to provide an appreciable effect of addition of the hydrogen peroxide. The temperature is selected to range preferably 0 to 100°C, more preferably 5 to 80°C and most preferably 5 to 60°C.

The porous Si after the etching was rinsed with water and the rinsed surface was examined by microanalysis by using secondary ions but no impurity was detected.

A description will now be given of the etching characteristics of porous Si and non-porous Si as observed when they are etched by a mixture solution of hydrofluoric acid and aqueous hydrogen peroxide, with specific reference to Fig. 6C. Fig. 6C shows the time dependencies of etched depth of porous Si and monocrystalline Si as observed when the porous Si and the monocrystalline Si are immersed in a mixture solution of hydrofluoric acid and aqueous hydrogen peroxide. The porous Si was formed by anodization of monocrystalline Si conducted under the same conditions as those shown before. The use of monocrystalline Si as the starting material for forming porous Si through anodization is only illustrative and Si of other crystalline structures can be used as the starting material.

A test piece of porous Si prepared as described above was immersed, followed by agitation, in a mixture solution of 49 % hydrofluoric acid and aqueous hydrogen peroxide (white circles), and reduction in the thickness of the porous Si was measured. The porous Si was rapidly etched: namely, by a thickness of 112 μm in 40 minutes and 256 μm in 80 minutes, with high degrees of surface quality and uniformity. Although the concentration of aqueous hydrogen peroxide was 30 % in this case, the concentration of hydrogen peroxide may be suitably determined within a range which does not impair the effect of addition of hydrogen peroxide and which does not cause any practical inconvenience in the production.

The etching rate depends on the concentration and the temperature of the hydrofluoric acid and aqueous hydrogen peroxide

The addition of hydrogen peroxide serves to accelerate oxidation of silicon, thus enhancing the reaction speed as compared to the case where hydrogen peroxide is not added. Furthermore, the reaction speed can be controlled by suitably selecting the content of the hydrogen peroxide.

A test piece of a non-porous Si of 500 μm thick was immersed in a mixture solution of 49 % hydrofluoric acid and aqueous hydrogen peroxide (1 : 5) (Black circles), followed by agitation of the solution. The reduction in th thickn ss of th porous Si was then measured. In this cas , th test piece of nonporous Si was etched only by 100 Angstrom or l ss even after elaps of 120 minutes. Th etching rate showed almost no dep ndency

on th solution concentration and temperature.

Both the porous and non-porous Si test pieces after the etching w re rins d with water and the surface states of thes test pieces w re examined by microanalysis with secondary ions but n impurity was detected.

Naturally, various embodim nts xplained in conn ction with I by making ref rence to Figs. 1A and 1B, Figs. 2A and 2B, Figs. 3A to 3C and Figs. 4A to 4C can be realized als in the cas where the mixture solution of hydrofluoric acid and aqu ous hydrog n peroxide is used as the etching solution.

I-(4)

A description will now be given of the case where a mixture of hydrofluoric acid, an alcohol and aqueous hydrogen peroxide is used as the electroless wet chemical etching solution for porous Si, with reference to Fig. 7D.

Fig. 7D shows the time dependency of etched thickness of porous Si as observed when the porous Si is immersed in a mixture liquid of hydrofluoric acid, ethyl alcohol and aqueous hydrogen peroxide without agitation of the liquid. The porous Si was formed by anodizing monocrystalline Si under the conditions shown below. The use of the monocrystalline Si as the starting material for forming the porous Si structure through anodization is only illustrative and Si of other crystalline structures can be used as the starting material.

Voltage applied: 2.6 (V)
Current density: 30 (mA·cm⁻²)
Anodizing solution: $HF:H_2O:C_2H_5OH = 1 : 1 : 1$
Time: 2.4 (hours)
Thickness of porous Si: 300 (μm)
Porosity: 56 (%)

Test pieces of the porous Si prepared as described above were immersed, without agitation, in a mixture solution of 49 % hydrofluoric acid, ethyl alcohol and aqueous hydrogen peroxide (10 : 6 : 50) (white circles) and in a mixture solution of 49 % hydrofluoric acid, ethyl alcohol and hydrogen peroxide (10 : 2 : 10) (black circles). The reductions in the thicknesses of the porous Si test pieces were then measured. Large rates of etching of the porous Si were observed: namely, in the case of the 10 : 6 : 50 solution, the porous Si was etched by 107 μm and, in case of the 10 : 2 : 10 solution, the porous Si was etched by 128 μm, in about 40 minutes. After elapse of 80 minutes, the porous Si was etched by a thickness as large as 244 μm in the case of the 10 : 6 : 50 solution and 292 μm in the case of the 10 : 2 : 10 solution, with high degrees of states of the etched surfaces. The concentration of aqueous hydrogen peroxide was 30 % in this case but the hydrogen peroxide concentration may be determined in a range which provides an appreciable effect of addition of hydrogen peroxide and which does not cause any practical problem in the production process.

The etching rate has dependencies on the density of the hydrofluoric acid solution, as well as on the temperature of the same. The addition of alcohol serves to accelerate oxidation of silicon, thus enhancing the reaction speed as compared to the case where hydrogen peroxide is not used. It is also possible to control the reaction speed by suitably selecting the content of hydrogen peroxide. On the other hand, the addition of alcohol serves to remove, without delay, bubbles of reaction gases generated as a result of the etching from the etched surface, without requiring agitation of the solution, thus offering high degrees of efficiency and uniformity of etching of the porous Si.

The solution density and the solution temperature are determined such that a practical etching speed is obtained and such that the effect of the use of hydrofluoric acid, alcohol and hydrogen peroxide is appreciable. Although the mixture solutions of 49 % hydrofluoric acid, ethyl alcohol and hydrogen peroxide (10 : 6 : 50) and 49 % hydrofluoric acid, ethyl alcohol and hydrogen peroxide (10 : 2 : 10), as well as the room temperature as the solution temperature, are mentioned, these solution densities and temperature are only illustrative and are not intended to restrict the scope of the invention.

The HF concentration with respect to the etching solution preferably ranges between 1 and 95 %, more preferably between 5 and 90 % and most preferably between 5 and 80 %. The concentration of H_2O_2 with respect to the etching solution is preferably selected to range between 1 and 95 %, more preferably between 5 and 90% and most preferably between 10 and 80%, and is determined so as to provide an appreciable effect of addition of the hydrogen peroxide. The concentration of the alcohol with respect to the etching solution is preferably determined to be 80 % or less, more preferably 60 % or less and most preferably 40 % or less, and is selected so as to provide an appreciable effect of addition of the alcohol. The temperature is selected to range preferably 0 to 100°C, more preferably 5 to 80°C and most preferably 5 to 60°C.

Alcohol to be used in the present invention is not limited to ethyl alcohol and includes those alcohols such as isopr pyl alc hol which can practically be used in preparation proc ss and accomplish th effect of the addition of alcoh l as mentioned above.

12

The porous Si after the etching was rins d with water and the rinsed surface was xamined by micro-analysis by using s condary ions but n impurity was d tected.

This type of etching solution is advantageous in that bubbl s of reaction product gases g n rated as a result of th etching can be remov d without delay from the surface being tch d, without requiring agitation, so that th surface is etched with high d grees of smoothness and uniformity ven to th bottoms of minute recess s which may xist in the tched surface.

A description will now be given of the etching characteristics of porous Si and non-porous Si as observed when they are etched by a mixture solution of hydrofluoric acid, ethyl alcohol and aqueous hydrogen peroxide, with specific reference to Fig. 6D.

Fig. 6D shows the time dependencies of etched thickness of porous Si and monocrystalline Si as observed when the porous Si and the monocrystalline Si are immersed in a mixture solution of hydrofluoric acid, ethyl alcohol and aqueous hydrogen peroxide, without agitation. The porous Si was formed by anodization of mono-crystalline Si conducted under the same conditions as those shown before. The use of monocrystalline Si as the starting material for forming porous Si throught anodization is only illustrative and Si of other crystalline structures can be used as the starting material.

A test piece of porous Si prepared as described above was immersed, without agitaion, in a mixture solution of 49 % hydrofluoric acid, ethyl alcohol and aqueous hydrogen peroxide (10 : 6 : 50) (white circles) at the room temperature, and reduction in the thickness of the porous Si was measured. The porous Si was rapidly etched: namely, by a thickness of 107 μm in 40 minutes and 244 μm in 80 minutes, with high degrees of surface quality and uniformity. Although the concentration of the aqueous hydrogen peroxide was 30 % in this case, the content of hydrogen perozide may be suitably determined within a range which does not impair the effect of addition of hydrogen peroxide and which does not cause any practical inconvenience in the production.

The etching rate depends on the concentration and the temperature of the hydrofluoric acid and aqueous hydrogen peroxide.

The addition of hydrogen peroxide serves to accelerate oxidation of silicon, thus enhancing the reaction speed as compared to the case where hydrogen peroxide is not added. Furthermore, the reaction speed can be controlled by suitably selecting the content of the hydrogen peroxide. In addition, alcohol serves to remove, without delay, bubbles of the reaction product gases generated as a result of the etching without requiring agi-tation, thus ensuring high degrees of uniformity and etching of the porous Si.

A test piece of a non-porous Si of 500 μm thick was immersed in a mixture solution of 49 % hydrofluoric acid, ethyl alcohol and aqueous hydrogen peroxide (10 : 6 : 50) (black circles) at the room temperature, without agitation of the solution. The reduction in the thickness was then measured. In this case, the test piece of non-porous Si was etched only by 100 Angstrom or less even after elapse of 120 minutes. The etching rate showed almost no dependency on the solution concentration and temperature.

Both the porous and non-porous Si test pieces after the etching were rinsed with water and the surface states of these test pieces were examined by microanalysis with secondary ions but no impurity was detected.

Naturally, the various embodiments explained in connection with I by making reference to Figs. 1A and 1B, Figs. 2A and 2B, Figs. 3A to 3C and Figs. 4A to 4C can be realized also in the case where the mixture solution of hydrofluoric acid, alcohol and aqueous hydrogen peroxide is used as the etchant for porous Si.

I-(5)

A description will now be given of the case where a buffered hydrofluoric acid is used as the electroless wet chemical etching solution for porous Si, with reference to Fig. 7E. For instance, an aqueous solution con-taining 36.2 % of ammonium fluoride (NH$_4$F) and 4.5 % of hydrogen fluoride (HF) is used as the buffered hyd-rofluoric acid.

Fig. 7E shows the time dependency of etching thickness of porous Si as observed when the porous Si is immersed in the buffered hydrofluoric acid followed by agitation. The porous Si was formed by anodizing mono-crystalline Si under the conditions shown below. The use of the monocrystalline Si as the starting material for forming the porous Si structure through anodization is only illustrative and Si of other crystalline structures can be used as the starting material.

Voltage applied:	2.6 (V)
Current density:	30 (mA·cm^{-2})
Anodizing solution:	HF:H$_2$O:C$_2$H$_5$OH = 1 : 1 : 1
Time:	2.4 (hours)
Thickness of porous Si:	300 (μm)
Porosity:	56 (%)

Test pi c s of th porous Si prepared as d scribed abov w re imm rs d, followed by agitation, in th

buffered hydrofluoric acid (white circles) and in a 20 % diluted buff red hydrofluoric acid (black circl s). Th reductions in th thickn sses of th porous Si test pieces w re then measured. Large rates of etching of th porous Si were obs rved: nam ly, in the cas of buff red hydrofluoric acid, the porous Si was etched by 70 μm and, in cas of the 20 % diluted buffered hydrofluoric acid, the porous Si was tch d by 56 μm, in about

5 40 minutes. After elaps of 120 minutes, th porous Si was tch d by a thickness as large as 118 μm in the cas of th buff red hydrofluoric acid and 94 μm in the case f th 20 % diluted buff red hydrofluoric acid, with high degrees of states of the etched surfaces.

The etching rate has dependencies on the density of the hydrofluoric acid solution, as well as on the temperature of the same. The density of the solution and the temperature of the same are determined to fall within

10 the ranges which would not cause any practical inconvenience. Although the buffered hydrofluoric acid which is an aqueous solution containing 36.2 % of ammonium fluoride (NH$_4$F) and 4.5 % of hydrogen fluoride (HF) and the 20 % diluted buffered hydrofluoric acid, as well as the room temperature as the solution temperature, are mentioned, these solution densities and temperature are only illustrative and are not intended to restrict the scope of the invention.

15 The HF concentration in the buffered hydrofluoric acid with respect to the etching solution preferably ranges between 1 and 95 %, more preferably between 1 and 85 % and most preferably between 1 and 70 %. The concentration of NH$_4$ in the buffered hydrofluoric acid with respect to the etching solution is preferably selected to range between 1 and 95 %, more preferably between 5 and 90% and most preferably between 5 and 80%. The temperature is selected to range preferably 0 to 100°C, more preferably 5 to 80°C and most preferably 5

20 to 60°C.

The porous Si after the etching was rinsed with water and the rinsed surface was examined by microanalysis by using secondary ions but no impurity was detected.

A description will now be given of the etching characteristics of porous Si and non-porous Si as observed when they are etched by the buffered hydrofluoric acid, with specific reference to Fig. 6E. Fig. 6E shows the

25 time dependencies of etching of porous Si and monocrystalline Si as observed when the porous Si and the monocrystalline Si are immersed in the buffered hydrofluoric acid. The porous Si was formed by anodization of monocrystalline Si conducted under the same conditions as those shown before. The use of monocrystalline Si as the starting material for forming porous Si through anodization is only illustrative and Si of other crystalline structures can be used as the starting material.

30 A test piece of porous Si prepared as described above was immersed, followed by agitation, in the buffered hydrofluoric acid (white circles) at the room temperature, and reduction in the thickness of the porous Si was measured. The porous Si was rapidly etched: namely, by a thickness of 70 μm in 40 minutes and 118 μm in 120 minutes, with high degrees of surface quality and uniformity.

The etching rate has dependencies on the density of the hydrofluoric acid solution, as well as on the tem-

35 perature of the same. The density of the solution and the temperature of the same are determined to fall within the ranges which would not cause any practical inconvenience. Although the buffered hydrofluoric acid which is an aqueous solution containing 36.2 % of ammonium fluoride (NH$_4$F) and 4.5 % of hydrogen fluoride (HF) as well as the room temperature as the solution temperature, are mentioned, these solution densities and temperature are only illustrative and are not intended to restrict the scope of the invention.

40 A test piece of a non-porous Si of 500 μm thickness was immersed in the buffered hydrofluoric acid(black circles) at the room temperature, followed by agitation of the solution. The reduction in the thickness was then measured. In this case, the test piece of non-porous Si was etched only by 100 Angstroms or less even after elapse of 120 minutes. The etching rate showed almost no dependency on the solution density and temperature.

45 Both the porous and non-porous Si test pieces after the etching were rinsed with water and the surface states of these test pieces were examined by microanalysis with secondary ions but no impurity was detected.

Obviously, various etching methods explained in connection with (1) by making reference to Figs. 1A and 1B, Figs. 2A and 2B, Figs. 3A to 3C and Figs. 4A to 4C can be realized also in the case where the buffered hydrofluoric acid is used as the etching solution.

50

I-(6)

A description will now be given of the case where a mixture liquid of a buffered hydrofluoric acid and an alcohol is used as the electroless wet chemical etching solution for porous Si, with reference to Fig. 7F. For

55 instance, an aqueous solution containing 36.2 % of ammonium fluoride (NH$_4$F) and 4.5 % of hydrogen fluoride (HF) is used as the buffered hydrofluoric acid.

Fig. 7F shows the time dependency of etching thickness of porous Si as observed wh n the porous Si is immersed in th mixed solution of the buff red hydroflu ric acid and thyl alcoh l, without agitation. Th porous

14

Si was f rmed by anodizing monocrystalline Si und r th conditions shown b low. The use of th monocrys-
talline Si as th starting material for forming the porous Si structure through anodization is only illustrativ and
Si of other crystalline structures can be used as the starting material.

Voltag appli d: 2.6 (V)
Curr nt d nsity: 30 (mA·cm⁻²)
Anodizing solution: $HF:H_2O:C_2H_5OH = 1 : 1 : 1$
Time: 2.4 (hours)
Thickness of porous Si: 300 (μm)
Porosity: 56 (%)

Test pieces of the porous Si prepared as described above were immersed, without agitation, in a mixture
solution of the buffered hydrofluoric acid and ethyl alcohol(10 : 1) (white circles) and in a mixture solution of
20 % diluted buffered hydrofluoric acid and ethyl alcohol (10 : 1) (black circles). The reductions in the thicknes-
ses of the porous Si test pieces were then measured. Large rates of etching of the porous Si were observed:
namely, in the case of the mixture solution of the buffered hydrofluoric acid and ethyl alcohol (10 : 1), the porous
Si was etched by 67 μm and, in case of the mixture solution of the 20 % diluted buffered hydrofluoric acid and
ethyl alcohol (10 : 1), the porous Si was etched by 54 μm, in about 40 minutes. After elapse of 120 minutes,
the porous Si was etched by a thickness as large as 112 μm in the case of the mixture solution of the buffered
hydrofluoric acid and ethyl alcohol (10 : 1) and 90 μm in the case of the mixture solution of 20 % diluted buffered
hydrofluoric acid and ethyl alcohol (10 : 1), with high degrees of states of the etched surfaces. The etching rate
has dependencies on the density of the hydrofluoric acid solution, as well as on the temperature of the same.
The addition of alcohol serves to remove, without delay, bubbles of reaction product gases generated as a result
of the etching from the surface being etched, without requiring agitation, thus enabling etching of the porous
Si with high degrees of uniformity and efficiency.

The density of the solution and the temperature of the same are determined to fall within the ranges which
would not cause any practical inconvenience. Although the mixture solution of the buffered hydrofluoric acid
and ethyl alcohol (10 : 1) and the mixture solution of the 20 % diluted buffered hydrofluoric acid and ethyl alcohol
(10 : 1), as well as the room temperature as the solution temperature, are mentioned, these solution densities
and temperature are only illustrative and are not intended to restrict the scope of the invention.

The HF concentration in the buffered hydrofluoric acid with respect to the etching solution preferably ranges
between 1 and 95 %, more preferably between 1 and 85 % and most preferably between 1 and 70 %. The con-
centration of NH_4 in the buffered hydrofluoric acid with respect to the etching solution is preferably selected to
range between 1 and 95 %, more preferably between 5 and 90% and most preferably between 5 and 80%.
The concentration of the alcohol with respect to the etching solution is preferably 80 % or less, more preferably
60 % or less and most preferably 40 % or less, and is determined to make the effect of addition of the alcohol
appreciable. The temperature is selected to range preferably 0 to 100°C, more preferably 5 to 80°C and most
preferably 5 to 60°C.

Although ethyl alcohol has been specifically mentioned, other alcohols such as isopropyl alcohol, which
does not cause any inconvenience in the commercial production and which can provide an appreciable effect
of addition of such alcohol, may be used as the alcohol used in this type of etching solution.

The porous Si after the etching was rinsed with water and the rinsed surface was examined by micro-
analysis by using secondary ions but no impurity was detected.

In this etching solution, bubbles of reaction product gases generated as a result of the etching can be
removed without delay and without requiring agitation of the solution, by virtue of the addition of the alcohol,
so that the bottoms of minute recesses can be formed with high degrees of smoothness and uniformity.

A description will now be given of the etching characteristics of porous Si and non-porous Si as observed
when they are etched by the mixture solution of the buffered hydrofluoric acid and the ethyl alcohol, with specific
reference to Fig. 6F. Fig. 6F shows the time dependencies of etching thickness of porous Si and monocrystalline
Si as observed when the porous Si and the monocrystalline Si are immersed in the mixture solution of the buf-
fered hydrofluoric acid and ethyl alcohol. The porous Si was formed by anodization of monocrystalline Si con-
ducted under the same conditions as those shown before. The use of monocrystalline Si as the starting material
for forming porous Si through anodization is only illustrative and Si of other crystalline structures can be used
as the starting material.

A test piece of porous Si prepared as described above was immersed, without agitation, in the mixture sol-
ution of the buffered hydrofluoric acid and ethyl alcohol (10 : 1) (white circles) at the room temperature, and
reduction in the thickness of the porous Si was measured. The porous Si was rapidly etched: namely, by a thick-
ness of 67 μm in 40 minutes and 112 μm in 120 minutes, with high degrees of surface quality and uniformity.

A t st piece of a n n-porous Si of 500 μm thickness was immers d in the mixture solution of the buff red
hydrofluoric acid and thyl alcohol (10 : 1) (black circles) at th room temperature, without agitation of th sol-

ution. The r duction in the thickness of th non-porous Si was then measured. In this cas , the test pi ce of non-porous Si was etched nly by 100 Angstroms or less v n aft r elaps f 120 minutes. The tching rate showed almost no dep ndency on th olution d nsity and temp rature.

Both th p rous and non-porous Si test pieces after the tching were rins d with water and th surface states of thes test pieces w re examined by microanalysis with secondary ions but no impurity was detected.

Obviously, various tching methods explained in connection with (1) by making reference to Figs. 1A and 1B, Figs. 2A and 2B, Figs. 3A to 3C and Figs. 4A to 4C can be realized also in the case where the mixture solution of the buffered hydrofluoric acid and alcohol is used as the etching solution.

I-(7)

A description will now be given of the case where a mixture solution of a buffered hydrofluoric acid and hydrogen peroxide is used as the electroless wet chemical etching solution for porous Si, with reference to Fig. 7G For instance, an aqueous solution containing 36.2 % of ammonium fluoride (NH$_4$F) and 4.5 % of hydrogen fluoride (HF) is used as the buffered hydrofluoric acid.

Fig. 7G shows the time dependency of etching thickness of porous Si as observed when the porous Si is immersed in the mixed solution of the buffered hydrofluoric acid and hydrogen peroxide followed by agitation. The porous Si was formed by anodizing monocrystalline Si under the conditions shown below. The use of the monocrystalline Si as the starting material for forming the porous Si structure through anodization is only illustrative and Si of other crystalline structures can be used as the starting material.

Voltage applied:	2.6 (V)
Current density:	30 (mA·cm^{-2})
Anodizing solution:	HF:H$_2$O:C$_2$H$_5$OH = 1 : 1 : 1
Time:	2.4 (hours)
Thickness of porous Si:	300 (μm)
Porosity:	56 (%)

Test pieces of the porous Si prepared as described above were immersed, followed by agitation, in a mixture solution of the buffered hydrofluoric acid and hydrogen peroxide (1 : 5) (white circles) and in a mixture solution of the buffered hydrofluoric acid and hydrogen peroxide (5 : 1) (black circles). The reductions in the thicknesses of the porous Si test pieces were then measured. Large rates of etching of the porous Si were observed: namely, in the case of the 1 : 5 mixture solution, the porous Si was etched by 88 μm and, in case of the 5 : 1 mixture solution, the porous Si was etched by 105 μm, in about 40 minutes. After elapse of 120 minutes, the porous Si was etched by a thickness as large as 147 μm in the case of the 1 : 5 mixture and 177 μm in the case of the 5 : 1 mixture solution, with high degrees of states of the etched surfaces. In this case, the concentration of hydrogen peroxide was 30 %. This, however, is only illustrative and the concentration of hydrogen peroxide is suitably selected within a range which does not impair the effect of addition of hydrogen peroxide. The etching rate has dependencies on the solution densities of the buffered hydrofluoric acid and hydrogen peroxide, as well as on the temperature of the same. The addition of hydrogen peroxide accelerates the oxidation of silicon, thus attaining a higher reaction speed as compared to the case where hydrogen peroxide is not added. In addition, the reaction speed can be controlled by suitably determining the content of hydrogen peroxide.

The density of the solution and the temperature of the same are determined to fall within the ranges which would not cause any practical inconvenience in commercial production. Although the mixture solution of the buffered hydrofluoric acid and hydrogen peroxide (1 : 5) and the mixture solution of the buffered hydrofluoric acid and hydrogen peroxide (5 : 1), as well as the room temperature as the solution temperature, are mentioned, these solution densities and temperature are only illustrative and are not intended to restrict the scope of the invention.

The HF concentration in the buffered hydrofluoric acid with respect to the etching solution preferably ranges between 1 and 95 %, more preferably between 1 and 85 % and most preferably between 1 and 70 %. The concentration of NH$_4$ in the buffered hydrofluoric acid with respect to the etching solution is preferably selected to range between 1 and 95 %, more preferably between 5 and 90% and most preferably between 5 and 80%. The concentration of H$_2$O$_2$ with respect to the etching solution is preferably 1 to 95 %, more preferably 5 to 90 % and most preferably 10 to 80 %, and is determined to make the effect of addition of the hydrogen peroxide. The temperature is selected to range preferably 0 to 100°C, more preferably 5 to 80°C and most preferably 5 to 60°C.

The porous Si after the etching was rinsed with water and the rinsed surface was examined by microanalysis by using secondary ions but no impurity was d tect d.

A d scription will now b giv n of th tching characteristics f porous Si and non-porous Si as obs rv d

wh n they ar etch d by the mixture solution of the buffered hydrofluoric acid and hydrogen peroxid , with specific refer nce to Fig. 6G. Fig. 6G shows the time d pendencies of etching thickness of porous Si and monocrystalline Si as bserved when th porous Si and th monocrystallin Si are immersed in the mixture soluti n of the buff red hydrofluoric acid hydrogen peroxid . The porous Si was formed by anodization of monocrystalline Si conducted und r th same conditi ns as those shown b fore. Th us of m nocrystallin Si as th starting material for forming porous Si through anodization is only illustrativ and Si of other crystallin structures can be used as the starting material.

A test piece of porous Si prepared as described above was immersed, followed by agitation, in the mixture solution of the buffered hydrofluoric acid and hydrogen peroxide (1 : 5) (white circles) at the room temperature, and reduction in the thickness of the porous Si was measured. The porous Si was rapidly etched: namely, by a thickness of 88 μm in 40 minutes and 147 μm in 120 minutes, with high degrees of surface quality and uniformity. Although in this case the concentration of hydrogen peroxide was 30 %, this is only illustrative and the content of hydrogen peroxide is suitably selected within a range which does not cause any practical inconvenience and which does not impair the effect produced by the addition of hydrogen peroxide.

Both the porous and non-porous Si test pieces after the etching were rinsed with water and the surface states of these test pieces were examined by microanalysis with secondary ions but no impurity was detected.

Obviously, various etching methods explained in connection with (1) by making reference to Figs. 1A and 1B, Figs. 2A and 2B, Figs. 3A to 3C and Figs. 4A to 4C can be realized also in the case where the mixture solution of the buffered hydrofluoric acid and alcohol is used as the etching solution.

I-(8)

The following will now be given of the case where a mixture solution of a buffered hydrofluoric acid, an alcohol and hydrogen peroxide is used as the electroless wet chemical etching solution for porous Si, with reference to Fig. 7H. For instance, an aqueous solution containing 36.2 % of ammonium fluoride (NH_4F) and 4.5 % of hydrogen fluoride (HF) is used as the buffered hydrofluoric acid.

Fig. 7H shows the time dependency of etching thickness of porous Si as observed when the porous Si is immersed in the mixed solution of the buffered hydrofluoric acid, ethyl alcohol and hydrogen peroxide without agitation. The porous Si was formed by anodizing monocrystalline Si under the conditions shown below. The use of the monocrystalline Si as the starting material for forming the porous Si structure through anodization is only illustrative and Si of other crystalline structures can be used as the starting material.

Voltage applied:	2.6 (V)
Current density:	30 ($mA \cdot cm^{-2}$)
Anodizing solution:	$HF:H_2O:C_2H_5OH = 1 : 1 : 1$
Time:	2.4 (hours)
Thickness of porous Si:	300 (μm)
Porosity:	56 (%)

Test pieces of the porous Si prepared as described above were immersed, without agitation, in a mixture solution of the buffered hydrofluoric acid, ethyl alcohol and hydrogen peroxide (10 : 6 : 50) (white circles) and in a mixture solution of the buffered hydrofluoric acid, ethyl alcohol and hydrogen peroxide (50 : 6 : 10) (black circles). The reductions in the thicknesses of the porous Si test pieces were then measured. Large rates of etching of the porous Si were observed: namely, in the case of the 10 : 6 : 50 mixture solution, the porous Si was etched by 83 μm and, in case of the 50 : 6 : 10 mixture solution, the porous Si was etched by 100 μm, in about 40 minutes. After elapse of 120 minutes, the porous Si was etched by a thickness as large as 140 μm in the case of the 10 : 6 : 50 mixture and 168 μm in the case of the 50 : 6 : 10 mixture solution, with high degrees of states of the etched surfaces. In this case, the concentration of hydrogen peroxide was 30 %. This, however, is only illustrative and the concentration of hydrogen peroxide is suitably selected within a range which does not impair the effect of addition of hydrogen peroxide. The etching rate has dependencies on the concentrations of the buffered hydrofluoric acid and hydrogen peroxide, as well as on the temperature of the same. The addition of hydrogen peroxide accelerates the oxidation of silicon, thus attaining a higher reaction speed as compared to the case where hydrogen peroxide is not added. In addition, the reaction speed can be controlled by suitably determining the ratio of hydrogen peroxide. The addition of alcohol enables bubbles of reaction products gases generated as a result of the etching to be removed from the surface being etched, without delay and without agitation, thus making it possible to etch the porous Si uniformly and with high efficiency.

The concentrations of the solution and the temperature of the solution are determined to fall within the ranges which provide the above effects of the use of the buffered hydrofluoric acid, hydrogen peroxide and the alcohol and which would not cause any practical inconvenience in commercial production. Although the mixture soluti n of the buffered hydrofluoric acid, ethyl alcohol and hydrogen peroxid (10 : 6 : 50) and th mixture sol-

ution f th buff red hydrofluoric acid, thyl alcohol and hydrog n peroxide (50 : 6 : 10), as w ll as the room temperature as th solution t mperature, are mention d, these solution ratio and temperature are only illustrative and are not intend d to restrict th scope of th invention.

Th HF concentration in th buffered hydrofluoric acid with respect to th tching solution preferably ranges betwe n 1 and 95 %, more pref rably b tween 1 and 85 % and most pref rably between 1 and 70 %. The concentration of NH_4F in th buffered hydrofluoric acid with respect to th etching s lution is pref rably selected to range between 1 and 95 %, more preferably between 5 and 90% and most preferably between 5 and 80%. The concentration of H_2O_2 with respect to the etching solution is preferably 1 to 95 %, more preferably 5 to 90 % and most preferably 10 to 80 %, and is determined to make the effect of addition of the alcohol appreciable. The concentration of the alcohol with respect to the etching solution is preferably 80 % or less, more preferably 60 % or less and most preferably 40 % or less, and is determined to make the effect of addition of the alcohol appreciable. The temperature is selected to range preferably 0 to 100°C, more preferably 5 to 80°C and most preferably 5 to 60°C.

Although ethyl alcohol has been specifically mentioned, other alcohols such as isopropyl alcohol, which does not cause any inconvenience in the commercial production and which can provide an appreciable effect of addition of such alcohol, may be used as the alcohol used in this type of etching solution.

The porous Si after the etching was rinsed with water and the rinsed surface was examined by micro-analysis by using secondary ions but no impurity was detected.

This etching solution enables bubbles of reaction product gases generated by the etching to be removed from the surface being etched, without delay and without requiring agitation, so that the etching can be performed with high degrees of smoothness and uniformity at the bottoms of minute recesses of the surface to be etched.

Clearly, embodiments explained in the above (1) by making reference to Figs. 1A and 1B, Figs. 2A and 2B, Figs. 3A to 3C and Figs. 4A to 4C can be realized also in the case where the mixture solution of the buffered hydrofluoric acid, alcohol and hydrogen peroxide is used as the etching solution.

II. The following will now be given of a process of the invention for producing a semiconductor member.

As explained before, the first embodiment of the process for producing the semiconductor member in accordance with the present invention has the following features.

Namely, the first embodiment of the process of the invention for producing a semiconductor member comprises the steps of: forming a member having a non-porous silicon monocrystalline layer and a porous silicon layer; bonding to the monocrystalline layer a member having an insulating material surface; and removing by etching the porous silicon layer by immersing it in hydrofluoric acid.

As explained before, the second embodiment of the process of the invention for producing a semiconductor member uses the same steps as those in the method of the first embodiment, except that, in place of the hydrofluoric acid used in the first embodiment, one of the second to eighth embodiment of the etching solutions mentioned before.

The third to sixth embodiments of the process of the invention for producing a semiconductor member, which also were explained before, are more practical embodiments of the first and the second embodiments of the process of the invention. The process of the present invention for producing a semiconductor member will be described hereinafter with reference to the third to sixth embodiments.

II-(1)

The third embodiment of the process of the invention for producing a semiconductor member will be described with reference to the drawings.

Embodiment 1

The following will be first given of a method in which the whole member is changed into porous structure and then a monocrystalline layer is formed on the porous structure by epitaxial growth method. Figs. 8A to 8C are schematic sectional views of the semiconductor member illustrating each of steps of the process.

Referring to Fig. 8A, as the first step, an Si monocrystalline semiconductor member 11 is prepared and is wholly changed into porous structure and, then, an epitaxial growth method is applied to one surface of the porous member, thereby forming a thin film of monocrystalline Si layer 12. The porous structure of Si member is formed by, for example, an anodization employing an HF soluti n. The initial monocrystallin Si having the density of 2.33 g/cm³ can b changed into a por us Si memb r th d nsity of which can be varied within th

18

range betw en 1.1 and 0.6 g/cm³ by varying the HF concentration of th etching solution betw n 50 % and 20 %.

Referring now to Fig. 8B, a light-transmissiv substrat 13, which is typically a glass sheet, is prepared and bond d on th surface of the monocrystalline Si layer 12 n th porous Si memb r. Subsequently, an Si₃N₄ lay r 14 is formed by d position as an anti-etching film to cov r th ntire member composed of the lay r 12 and the substrat 13 and the Si₃N₄ layer on th porous Si memb r 11 is removed. Although Si₃N₄ layer is suitably used as the anti-etching layer, it is possible to use other materials such as Apiezon wax as the material of the anti-etching layer. The porous Si member 11 is then immersed in the etching solution of the present invention and the solution is agitated so that only the porous Si is etched by electroless chemical etching, whereby a thinned non-porous monocrystalline silicon layer 12 is left on the light-transmissive substrate 13.

Fig. 8C shows the semiconductor member obtained by the present process. It will be said that, as a result of the removal of the anti-etching Si₃N₄ layer 14 in the step shown in Fig. 8B, a monocrystalline Si layer 12 having a crystallinity equivalent to that of a silicon wafer is formed on the light-transmissive substrate 13 with high degrees of smoothness and uniformity and with a small thickness, over a wide area covering the whole surface of the wafer.

The semiconductor member thus obtained is advantageous from the view point of production of an insulation-isolated electronic device.

Embodiment 2

The following will now be given of a process in which an N-type layer is formed before changing the initial member into porous structure and, subsequently to the formation of the P-type layer, a selective anodization is effected to change only the P-type substrate into porous structure.

Referring to Fig. 9A, as the first step, a layer 32 of a low impurity concentration is formed on the surface of a P-type Si monocrystalline substrate 31, by an epitaxial growth. Alternatively, an N-type monocrystalline layer 32 may be formed on the surface of the P-type Si monocrystalline substrate 31 by ion-implantation of proton.

Then, as shown in Fig. 9B, the P-type Si monocrystalline substrate 31 is changed into a porous Si substrate 33 by effecting, on the reverse side of the P-type Si monocrystalline substrate 31, an anodization using, for example, an HF solution. The initial monocrystalline Si having the density of 2.33 g/cm³ can be changed into a porous member the density of which can be varied within the range between 1.1 and 0.6 g/cm³ by varying the HF concentration of the etching solution between 50 % and 20 %.

Referring now to Fig. 9C, a light-transmissive substrate 34, which is typically a glass sheet, is prepared and bonded on the surface of the monocrystalline Si layer 32 on the porous Si member. Subsequently, an Si₃N₄ layer 35 is formed by deposition as an anti-etching film to cover the entire member composed of the layer 32 and the substrate 34 and the Si₃N₄ layer on the porous Si member 33 is removed. Although Si₃N₄ layer is suitably used as the anti-etching layer, it is possible to use other materials such as Apiezon wax as the material of the anti-etching layer. The porous Si substrate 33 is then immersed in the etching solution of the present invention and the solution is agitated so that only the porous Si is etched by electroless chemical etching, whereby a thinned non-porous monocrystalline silicon layer 32 is left on the light-transmissive substrate 34.

Fig. 9D shows the semiconductor member obtained by the present process. That is, as a result of the removal of the anti-etching Si₃N₄ layer in the step shown in Fig. 9D, a monocrystalline Si layer 32 having a crystallinity equivalent to that of a silicon wafer is formed on the light-transmissive substrate 34 with high degrees of smoothness and uniformity and with a small thickness, over a wide area covering the whole surface of the wafer.

The semiconductor member thus obtained is advantageous from the view point of production of an insulation-isolated electronic device.

According to the result of an observation by a transmission electron microscope, micro-pores of an average diameter of about 600 Angstrom are formed in the porous Si layer, so that the density of the layer has been reduced half or below that of the monocrystalline Si.

Nevertheless, the monocrystallinity is still maintained, so that it is possible to form a monocrystalline Si layer on the porous layer by epitaxial growth. When the temperature exceeds 1000°C, rearrangement of internal pores occurs, which impedes the acceleration of the etching. For this reason, the epitaxial growth of the Si layer is preferably effected by a low-temperature growth method such as, for example, a molecule-ray epitaxial growth method, a CVD method such as plasma CVD method, low-pressure CVD method or photo-CVD method, a bias sputter method or a liquid-phase growth method.

II-(2)

Th fourth mbodiment of the process of the inv ntion of producing a s miconductor member will be d s-
cribed with reference to the drawings.

5

Embodim nt 1

The following will be first given of a form in which the whole P- or high-density N-type substrate is changed
into porous structure and then a monocrystalline layer is formed on the porous structure by epitaxial growth
method Figs. 10A to 10C are schematic sectional views of the semiconductor member illustrating each of steps
of the process.

Referring to Fig. 10A, as the first step, an Si monocrystalline semiconductor member 11 of P-type (or high-
density N-type) is prepared and is wholly changed into porous structure and, then, an epitaxial growth is effected
by a suitable method on the surface of the porous member, thereby forming a thin film of monocrystalline Si
layer 12. The porous structure is formed by, for example, an anodization employing an HF solution. The initial
monocrystalline Si having the density of 2.33 g/cm^3 can be changed into a porous member the density of which
can be varied within the range between 1.1 and 0.6 g/cm^3 by varying the HF concentration of the etching solution
between 50 % and 20 %.

Referring now to Fig. 10B, another Si substrate 13 is prepared and an insulating layer (silicon oxide layer)
14 is formed on the surface of this Si substrate 13. Subsequently, the surface of the insulating layer 14 of the
Si substrate 13 is bonded to the surface of the monocrystalline layer 12 on the porous Si substrate. The whole
structure 11-14 composed of the substrates and layers to 14 is then immersed in the etching solution of the
present invention and the solution is agitated so that only the porous Si is etched by electroless wet chemical
etching, whereby a thinned non-porous monocrystalline silicon layer 12 is left on the insulating layer 14.

Fig. 10C shows the semiconductor member obtained by the present process. That is, the monocrystalline
Si layer 12 having a crystallinity equivalent to that of a silicon wafer is formed on the insulating layer 14 on the
Si substrate 13 with high degrees of smoothness and uniformity and with a small thickness, over a wide area
covering the whole surface of the wafer.

The semiconductor member thus obtained is advantageous from the view point of production of an insu-
lation-isolated electronic device.

Embodiment 2

The following will now be given of a process in which an N-type layer is formed before changing the initial
member into porous structure and, subsequently to the formation of the N-type layer, a selective anodization
is effected to change only the P-type substrate or the high-density N-type substrate into porous structure. Figs.
11A to 11D show, in schematic sectional views, the semiconductor member in different steps of the production
process.

Referring to Fig. 11A, as the first step, a layer 22 of a low impurity concentration is formed on the surface
of a P-type (or high-density N-type) Si monocrystalline substrate 21, by an epitaxial growth performed by a suit-
able method. Alternatively, an N-type monocrystalline layer 22 may be formed on the surface of the P-type Si
monocrystalline substrate 21 by ion-implantation of proton.

Then, as shown in Fig. 11B, the P-type Si monocrystalline substrate 21 is changed into a porous Si sub-
strate 23 by effecting, on the reverse side of the P-type monocrystalline substrate 21, an anodization using,
for example, an HF solution. The initial monocrystalline Si having the density of 2.33 g/cm^3 can be changed
into a porous member the density of which can be varied within the range between 1.1 and 0.6 g/cm^3 by varying
the HF concentration of the etching solution between 50 % and 20 %.

Referring now to Fig. 11C, another Si substrate 24 is prepared and an insulating layer 25 (silicon oxide
layer) is formed on the surface of the Si substrate 24. Then, the insulating layer 25 on the Si substrate 24 is
bonded to the surface of the monocrystalline Si layer 22 on the porous substrate. Subsequently, the whole struc-
ture composed of the substrates and layers 22 to 25 is immersed in the etching solution of the present invention
and the solution is agitated so that only the porous Si is etched by electroless chemical etching, whereby a
thinned non-porous monocrystalline silicon layer 22 is left on the insulating layer 25.

Fig. 11D shows the semiconductor member obtained by the present process. That is, a monocrystalline
Si layer 22 having a crystallinity equivalent to that of a silicon wafer is formed on the insulating layer 25 with
high degrees of smoothness and uniformity and with a small thickness, over a wide area covering the whole
surface f the wafer.

Th semiconductor member thus obtained is advantageous from th vi w point of production of an insu-

lation-is lated electronic d vic .

II-(3)

5   The fifth embodiment of th process of th invention will b described with reference to th drawings. A description will be first given of a form in which th whol Si substrat is changed into porous structure and then a monocrystalline layer is formed on the porous structure by epitaxial growth method.

Referring to Fig. 12A, as the first step, an Si monocrystalline substrate 11 is prepared and is wholly changed into porous structure and, then, an epitaxial growth is effected by a suitable method on the surface of the porous substrate, thereby forming a thin film monocrystalline layer 12. The porous structure is formed by, for example,
10   an anodization employing an HF solution. The initial monocrystalline Si having the density of 2.33 g/cm³ can be changed into a porous Si layer the density of which can be varied within the range between 1.1 and 0.6 g/cm³ by varying the HF concentration of the etching solution between 50 % and 20 %. The porous layer is tended to form in a P type Si substrate. A transmission electromicroscopic observation showed that the porous
15   Si layer thus formed has micropores of a mean diameter of about 600 Angstroms.

Referring now to Fig. 12B, a light-transmissive substrate 13, which is typically a glass sheet, is prepared. Then, the surface of the monocrystalline Si layer on the porous Si substrate is oxidized to form an oxide layer 14. The above-mentioned light-transmissive substrate 13 is then bonded on the surface of the oxide layer 14. This oxide layer plays an important role formation of device. Namely, with such an oxide layer, the interface
20   level generated at the interface under the Si active layer can be made lower as compared with the glass interface, so that the characteristics of the electronic device can be remarkably improved.

Referring further to Fig. 12B, and Si₃N₄ layer 15 is deposited as an anti-etching film(protective material) to cover the entire member composed of the two substrates bonded together, and the Si₃N₄ layer on the surface of porous Si substrate is removed. Although Si₃N₄ layer is suitably used as the anti-etching layer, it is possible
25   to use other materials such as Apiezon wax as the material of the anti-etching layer. The porous Si substrate 11 is then immersed in the etching solution of the present invention with agitating so that only the porous Si is etched by electroless chemical etching, whereby a thinned monocrystalline silicon layer is left on the light-transmissive substrate 13.

Fig. 12C shows the semiconductor member obtained by the described process. It will be seen that, as a
30   result of the removal of the anti-etching Si₃N₄ layer 15 in the step shown in Fig. 12B, a monocrystalline Si layer 12 having a crystallinity equivalent to that of a silicon wafer is formed on the light-transmissive substrate 13 with high degree of smoothness and uniformity and with a small thickness, over a wide area covering the whole surface of the wafer.

The semiconductor member thus obtained is advantageous from the view point of production of an insu-
35   lation-isolated electronic device.

II-(4)

          The sixth embodiment of the process of the invention for producing a semiconductor member will now be
40   described.

Embodiment 1

          A description will be first given of a form in which the whole Si substrate is changed into porous structure
45   and then a monocrystalline layer is formed by epitaxial growth method.

Figs. 13A to 13C illustrate successive steps of the first embodiment in accordance with the invention.

Referring to Fig. 13A, as the first step, an Si monocrystalline substrate is prepared and is wholly changed into porous structure (11). Then, an epitaxial growth is effected by a suitable method on the surface of the porous substrate, thereby forming a thin film of monocrystalline layer 12. The porous structure is formed by, for
50   example, an anodization employing an HF solution. The initial monocrystalline Si having the density of 2.33 g/cm³ can be changed into a porous Si layer the density of which can be varied within the range between 1.1 and 0.6 g/cm³ by varying the HF concentration of the etching solution between 50 % and 20 %. A transmission electromicroscopic observation showed that the porous Si layer thus formed has micropores of a mean diameter of about 600 Angstroms.

55   Referring now to Fig. 13B, another Si substrate 13 is prepared and an insulating material 14 is formed on the surface. Then the Si substrate having the insulating material 14 is bonded to the surface of an oxide layer 15 which is formed on th monocrystalline Si layer carri d by the por us Si substrate. The insulating material 14 may be a deposited silicon oxide, nitride, nitrided oxide, r tantalum, n t to mention the insulating layer of

Si. Th bonding step may b conducted by adh ring closely the rinsed surfac s, and heating both substrate in an oxyg n atmosph re or a nitrog n atmosph re. Th oxid layer 15 is formed for the purpose of reducing th interface level of the monocrystallin layer 12 which is the final active layer.

Th n, as shown in Fig. 13C, th porous Si substrate 11 is immersed in the tching solution of the pres nt invention and th solution is agitated, so that nly the porous Si is tched by lectroless wet ch mical tching so as to l av a thinned monocrystallin Si lay r on the insulating mat rial. Fig. 13C shows the semiconductor substrate obtained according to the present invention. As a result, a monocrystalline Si layer 12 having crystallinity equivalent to that of a silicon wafer is formed on the insulated substrate 13 through the intermediary of the insulating material 14 and the oxide layer l5, with high degrees of smoothness and uniformity and with a small thickness over a wide area covering the whole surface of the wafer.

The semiconductor member thus obtained is advantageous from the view point of production of an insulation-isolated electronic device.

Embodiment 2

A second embodiment will be described with reference to the drawings.

Figs. 14A to 14D show, in schematic sectional views, the second embodiment according to the present invention.

Referring to Fig. 14A, as the first step, a layer 32 of a low impurity concentration is formed on the surface of a P-type Si monocrystalline substrate 31, by an epitaxial growth performed by a suitable method. Alternatively, an N-type monocrystalline layer 32 may be formed on the surface of the P-type Si monocrystalline substrate 21 by implantation of proton.

Then, as shown in Fig. 14B, the P-type Si monocrystalline substrate 31 is changed into a porous Si substrate 33 by effecting, on the reverse side of the P-type Si monocrystalline substrate 31 by anodization using, for example, an HF solution. The initial monocrystalline Si having the density of 2.33 g/cm^3 can be changed into a porous member the density of which can be varied within the range between 1.1 and 0.6 g/cm^3 by varying the HF concentration of the etching solution between 50 % and 20 %. As explained before, this porous layer is formed in the P-type substrate.

Referring now to Fig. 14C, another Si substrate 34 is prepared and an insulating layer 35 is formed on the surface of the Si substrate 34. Then, the Si substrate 34 having the insulating layer 35 is bonded to the surface of the oxide layer 36 formed on the monocrystalline Si layer on the porous Si substrate. Then, the porous Si substrate is immersed in the etching solution of the present invention and the solution is agitated so that only the porous Si is etched by electroless chemical etching, whereby a thinned non-porous monocrystalline silicon layer is left on the insulating layer.

Fig. 14D shows the semiconductor substrate obtained by the described process. It will be seen that a monocrystalline Si layer 32 having a crystallinity equivalent to that of a silicon wafer is formed on the insulated substrate 34 through the intermediary of the oxide layer 36 and the insulation layer 35, with high degrees of smoothness and uniformity and with a small thickness, over a wide area covering the whole surface of the wafer.

The semiconductor member thus obtained is advantageous from the view point of production of an insulation-isolated electronic device.

The processes described above are the type in which the N-type layer is formed prior to changing into porous structure and then only the P-type substrate is selectively changed into porous structure by anodization.

III. The present invention will be described below in detail by way of examples. However, the invention is not limited to these examples except as defined in the appended claims.

Example 1

A porous Si layer 21 was formed to a thickness of 50 μm (t_2 = 50 μm) on the entirety of one of the major surfaces of a monocrystalline Si substrate 22 by anodization (Fig. 1A).

Anodization was performed under the following conditions:

Applied voltage:	2.6 (V)
Current density:	30 (mA·cm^{-2})
Anodizing solution:	HF:H_2O:C_2H_5OH = 1:1:1
Time:	0.4 (hour)
Thickness of porous Si:	50 (μm)
Porosity:	56 (%)

Th r aft r, th p rous Si/monocrystallin Si substrat was subj cted to selective tching using a 49% HF

solution. In thirty-thre minutes, the porous Si was s lectively tched with the monocrystalline Si acting as an etch stopp r, only th monocrystalline Si being l ft b hind, as hown in Fig. 1B.

Exampl 2

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Prior t anodization, boron ions were implanted in ne of th surfaces of a monocrystallin Si substrate 32 at an average concentration of 1.0×10^{19} cm^{-3} in stripes spaced apart from each other by a distance of 100 ym. As shown in Fig. 2A, porous Si 31 was formed by anodization in stripes spaced apart from each other by a distance (b_3 = 100 μm) of 100 μm, each stripe having a width (a_3 = 100 μm) of 100 μm and a thickness (t_3 = 10 1 μm) of 1 μm.

Anodization was performed under the following conditions:

Applied voltage:	2.6 (V)
Current density:	30 (mA·cm^{-2})
Anodizing solution:	HF:H$_2$O:C$_2$H$_5$OH = 1:1:1
15 Thickness of porous Si:	1 (μm)
Porosity:	56 (%)

Thereafter, the porous Si/monocrystalline Si substrate was subjected to selective etching using a 49% HF solution. In two minutes, the porous Si was selectively etched, only the monocrystalline Si being left behind, as shown in Fig. 2B.

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Example 3

A 3μm (u_4 = 3 μm) thick polycrystalline Si layer 41 was formed on a monocrystalline Si substrate 42 by CVD (Fig. 3A). As shown in Fig. 3B, a surface layer of 2 μm (t_4 = 2 μm) of the polycrystalline Si layer 41 was 25 made porous by anodization to form a porous Si layer 43.

Anodization was performed under the following conditions:

Applied voltage:	2.6 (V)
Current density:	30 (mA·cm^{-2})
Anodizing solution:	HF:H$_2$O:C$_2$H$_5$OH = 1:1:1
30 Thickness of porous Si:	2 (μm)
Porosity:	56 (%)

Thereafter, the porous Si/polycrystalline Si/monocrystalline Si substrate was subjected to selective etching using a 49% HF solution. In four minutes, the porous Si was selectively etched with the polycrystalline Si acting as an etch stopper, only the polycrystalline Si and monocrystalline Si being left behind, as shown in Fig. 3C.

35

Example 4

A 3μm (u_5 = 3 μm) thick polycrystalline Si layer 51 was formed on a monocrystalline Si substrate 52 by CVD. Prior to anodization, boron ions were implanted into the surface of the polycrystalline Si layer 51 at 1.0 40 x 10^{19} cm^{-3} in stripes spaced apart from each other by a distance of 20 μm. As shown in Fig. 4A, porous Si 53 was formed by anodization in stripes spaced apart from each other by a distance (b_5 = 20 μm) of 20 μm, each stripe having a width (a_5 = 20 μm) of 20 μm and a thickness (t_5 = 1 μm) of 1 μm.

Anodization was performed under the following conditions:

Applied voltage:	2.6 (V)
45 Current density:	30 (mA·cm^{-2})
Anodizing solution:	HF:H$_2$O:C$_2$H$_5$OH = 1:1:1
Thickness of porous Si:	1 (μm)
Porosity:	56 (%)

Thereafter, the porous Si/polycrystalline Si/monocrystalline Si substrate was subjected to selective etching 50 using a 49% HF solution. In two minutes, the porous Si was selectively etched, only the polycrystalline Si and monocrystalline Si being left behind, as shown in Fig. 4B.

Example 5

55 A porous Si layer 61 was formed to a thickness of 50 μm (t_6 = 50 μm) on the entirety of one of the major surfaces of a monocrystalline Si suhstrate 62 by anodization (Fig. 5A).

Anodization was p rform d und r th following conditi ns:

Appli d voltage: 2.6 (V)

Current density:	30 (mA·cm^{-2})
Anodizing solution:	HF:H$_2$O:C$_2$H$_5$OH = 1:1:1
Time:	0.4 (hour)
Thickness of porous Si:	50 (μm)
Porosity:	56 (%)

As shown in Fig. 5B, a resist 63 was patterned in stripes spaced apart from each other by a distance (b_6 = 100 μm) of 100 μm, each stripe having a width (a_6 = 100 μm) of 100 μm.

Thereafter, the porous Si/monocrystalline Si substrate was subjected to selective etching using a 49% HF solution. In thirty-three minutes, the porous Si was selectively removed, only the monocrystalline Si being left behind, as shown in Fig. 5C. Finally, the resist was removed (Fig. 5D).

Example 6

Etching was performed in the same manner as that of Example 1 with the exception that a mixture solution (10:1) of 49% hydrofluoric acid and ethyl alcohol was used as an etchant. In twenty-nine minutes after initialization of etching, the porous Si was selectively removed with the monocrystalline Si acting as an etch stopper.

Example 7

Etching was performed in the same manner as that of Example 2 with the exception that a mixture solution (10:1) of 49% hydrofluoric acid and ethyl alcohol was used as an etchant. In one point seven minutes after initialization of etching, the porous Si was selectively removed, only the monocrystalline Si being left behind.

Example 8

Etching was performed in the same manner as that of Example 3 with the exception that a mixture solution (10:1) of 49% hydrofluoric acid and ethyl alcohol was used as an etchant. In three point four minutes after initialization of etching, the porous Si was selectively removed with the polycrystalline Si acting as an etch stopper, only the polycrystalline Si and the monocrystalline Si being left behind, as shown in Fig. 3C.

Example 9

Etching was performed in the same manner as that of Example 4 with the exception that a mixture solution (10:1) of 49% hydrofluoric acid and ethyl alcohol was used as an etchant. In one point seven minutes after initialization of etching, the porous Si was selectively removed, only the polycrystalline Si and monocrystalline Si being left behind, as shown in Fig. 4B.

Example 10

Etching was performed in the same manner as that of Example 5 with the exception that a mixture solution (10:1) of 49% hydrofluoric acid and ethyl alcohol was used as an etchant. In twenty-nine minutes after initialization of etching, the porous Si was selectively removed, only the monocrystalline Si being left behind, as shown in Fig. 5C. Finally, the resist was removed (Fig. 5D).

Example 11

Etching was performed in the same manner as that of Example 1 with the exception that a mixture solution (1:5) of 49% hydrofluoric acid and hydrogen peroxide was used as an etchant. In twenty-one minutes after initialization of etching, the porous Si was selectively removed with the monocrystalline Si acting as an etch stopper, only the monocrystalline Si being left behind, as shown in Fig. 1B.

Example 12

Etching was performed in the same manner as that of Example 2 with the exception that a mixture solution (1:5) of 49% hydrofluoric acid and hydrogen peroxide was used as an etchant. In one point three minutes after initialization of etching, the porous Si was selectively removed, only the monocrystalline Si being left behind, as shown in Fig. 2B.

Exampl 13

Etching was p rformed in the sam manner as that of Example 3 with the exception that a mixture solution (1:5) of 49% hydrofluoric acid and hydrogen peroxid was used as an etchant. In two point six minutes after
5 initialization of etching, the porous Si was sel ctively removed with th polycrystalline Si acting as an etch stopper, only the polycrystalline Si and the monocrysta11ine Si being left behind, as shown in Fig. 3C.

Example 14

10 Etching was performed in the same manner as that of Example 4 with the exception that a mixture solution (1:5) of 49% hydrofluoric acid and hydrogen peroxide was used as an etchant. In one point three minutes after initialization of etching, only the porous Si was selectively removed, only the polycrystalline Si and monocrystalline Si being left behind, as shown in Fig. 4B.

15 Example 15

Etching was performed in the same manner as that of Example 5 with the exception that a mixture solution (1:5) of 49% hydrofluoric acid and hydrogen peroxide was used as an etchant. In this etching, only the porous Si was selectively removed, leaving the monocrystalline Si behind, as shown in Fig. 5C. Finally, the resist was
20 removed (Fig. 5D).

Example 16

Etching was performed in the same manner as that of Example 1 with the exception that a mixture solution
25 (10:6:50) of 49% hydrofluoric acid, ethyl alcohol and hydrogen peroxide was used as an etchant. In twenty-six minutes after initialization of etching, the porous Si was selectively removed with the remaining monocrystalline Si acting as an etch stopper, as shown in Fig. 1B.

Example 17
30
Etching was performed in the same manner as that of Example 2 with the exception that a mixture solution (10:6:50) of 49% hydrofluoric acid, ethyl alcohol and hydrogen peroxide was used as an etchant. In one point four minutes after initialization of etching, the porous Si was selectively removed, only the monocrystalline Si being left behind, as shown in Fig. 2B.
35
Example 18

Etching was performed in the same manner as that of Example 3 with the exception that a mixture solution (10:6:50) of 49% hydrofluoric acid, ethyl alcohol and hydrogen peroxide was used as an etchant. In two point
40 eight minutes after initialization of etching, the porous Si was selectively removed with the polycrystalline Si acting as an etch stopper, only the polycrystalline Si and the monocrystalline Si being left behind, as shown in Fig. 3C.

Example 19
45
Etching was performed in the same manner as that of Example 4 with the exception that a mixture solution (10:6:50) of 49% hydrofluoric acid, ethyl alcohol and hydrogen peroxide was used as an etchant. In one point four minutes after initialization of etching, the porous Si was selectively removed, only the polycrystalline Si and monocrystalline Si being left behind, as shown in Fig. 4B.
50
Example 20

Etching was performed in the same manner as that of Example 5 with the exception that a mixture solution (10:6:50) of 49% hydrofluoric acid, ethyl alcohol and hydrogen peroxide was used as an etchant. In twenty-eight
55 minutes after initialization of etching, the porous Si was selectively removed, only the monocrystalline Si being left behind, as shown in Fig. 5C. Finally, the resist was removed (Fig. 5D).

Example 21

Etching was performed in the same manner as that of Example 1 with th xception that a buffered hydroflu ric acid (NH$_4$F: 36.2%, HF: 4.5%) was used as an tchant. In nin te n minutes after initialization of tching, th porous Si was s lectiv ly removed with the monocrystalline Si acting as an etch stopp r, as shown in Fig. 1B.

Example 22

Etching was performed in the same manner as that of Example 2 with the exception that a buffered hydrofluoric acid (NH$_4$F: 36.2%, HF: 4.5%) was used as an etchant. In seven seconds after initialization of etching, only the porous Si was selectively removed, leaving the monocrystalline Si behind, as shown in Fig. 2B.

Example 23

Etching was performed in the same manner as that of Example 3 with the exception that a buffered hydrofluoric acid (NH$_4$F: 36.2%, HF: 4.5%) was used as an etchant. In fourteen seconds after initialization of etching, the porous Si was selectively removed with the polycrystalline Si acting as an etch stopper, only the polycrystalline Si and the monocrystalline Si being left behind, as shown in Fig. 3C.

Example 24

Etching was performed in the same manner as that of Example 4 with the exception that a buffered hydrofluoric acid (NH$_4$F: 36.2%, HF: 4.5%) was used as an etchant. In seven seconds after initialization of etching, only the porous Si was selectively removed, leaving the polycrystalline Si and monocrystalline Si behind, as shown in Fig. 4B.

Example 25

Etching was performed in the same manner as that of Example 5 with the exception that a buffered hydrofluoric acid (NH$_4$F: 36.2%, HF: 4.5%) was used as an etchant. In nineteen minutes after initialization of etching, the porous Si was selectively removed, only the monocrystalline Si being left behind, as shown in Fig. 5C. Finally, the resist was removed (Fig. 5D).

Example 26

Etching was performed in the same manner as that of Example 1 with the exception that a mixture solution (10:1) of buffered hydrofluoric acid and ethyl alcohol was used as an etchant. In twenty-one minutes after initialization of etching, the porous Si was selectively removed with the monocrystalline Si acting as an etch stopper, only the monocrystalline Si being left behind, as shown in Fig. 1B.

Example 27

Etching was performed in the same manner as that of Example 2 with the exception that a mixture solution (10:1) of buffered hydrofluoric acid and ethyl alcohol was used as an etchant. In seven seconds after initialization of etching, only the porous Si was selectively removed, leaving the monocrystalline Si behind, as shown in Fig. 2B.

Example 28

Etching was performed in the same manner as that of Example 3 with the exception that a mixture solution (10:1) of buffered hydrofluoric acid and ethyl alcohol was used as an etchant. In fourteen seconds after initialization of etching, the porous Si was selectively removed with the polycrystalline Si acting as an etch stopper, only the polycrystalline Si and the monocrystalline Si being left behind, as shown in Fig. 3C.

Example 29

Etching was performed in the same manner as that of Example 4 with the xception that a mixture soluti n

(10:1) of buffered hydrofluoric acid and ethyl alcohol was used as an tchant. In s ven seconds after initiali-
zation of etching, only the porous Si was s lectively remov d, leaving the polycrystallin Si and m nocrystalline
Si behind, as shown in Fig. 4B.

5   Example 30

Etching was performed in the same manner as that of Example 5 with the exception that a mixture solution
(10:1) of buffered hydrofluoric acid and ethyl alcohol was used as an etchant. In twenty-one minutes after initiali-
zation of etching, the porous Si was selectively removed, only the monocrystalline Si being left behind, as shown
10 in Fig. 5C. Finally, the resist was removed (Fig. 5D).

Example 31

Etching was performed in the same manner as that of Example 1 with the exception that a mixture solution
15 (1:5) of buffered hydrofluoric acid and hydrogen peroxide was used as an etchant. In nine minutes after initiali-
zation of etching, the porous Si was selectively removed with the monocrystalline Si acting as an etch stopper,
only the monocrystalline Si being left behind, as shown in Fig. 1B.

Example 32

20
Etching was performed in the same manner as that of Example 2 with the exception that a mixture solution
(1:5) of buffered hydrofluoric acid and hydrogen peroxide was used as an etchant. In five seconds after initiali-
zation of etching, only the porous Si was selectively removed, leaving the monocrystalline Si behind, as shown
in Fig. 2B.

25
Example 33

Etching was performed in the same manner as that of Example 3 with the exception that a mixture solution
(1:5) of buffered hydrofluoric acid and hydrogen peroxide was used as an etchant. In ten seconds after initiali-
30 zation of etching, the porous Si was selectively removed with the polycrystalline Si acting as an etch stopper,
only the polycrystalline Si and the monocrystalline Si being left behind, as shown in Fig. 3C.

Example 34

35 Etching was performed in the same manner as that of Example 4 with the exception that a mixture solution
(1:5) of buffered hydrofluoric acid and hydrogen peroxide was used as an etchant. In five seconds after initiali-
zation of etching, only the porous Si was selectively removed, leaving the polycrystalline Si and monocrystalline
Si behind, as shown in Fig. 4B.

40 Example 35

Etching was performed in the same manner as that of Example 5 with the exception that a mixture solution
(1:5) of buffered hydrofluoric acid and hydrogen peroxide was used as an etchant. In nine minutes, the porous
Si was selectively removed, only the monocrystalline Si being left behind, as shown in Fig. 5C. Finally, the resist
45 was removed (Fig. 5D).

Example 36

Etching was performed in the same manner as that of Example 1 with the exception that a mixture solution
50 (10:6:50) of buffered hydrofluoric acid (NH_4F: 36.2%, HF 4.5%), ethyl alcohol and hydrogen peroxide was used
as an etchant. In ten minutes after initialization of etching, the porous Si was selectively removed with the mono-
crystalline Si acting as an etch stopper, only the monocrystalline Si being left, as shown in Fig. 1B.

Example 37

55
Etching was performed in the same manner as that of Example 2 with the exception that a mixture solution
(10:6:50) of buffered hydrofluoric acid (NH_4F: 36.2%, HF 4.5%), ethyl alcohol and hydrogen peroxide was used
as an etchant. In six seconds after initialization of tching, nly th porous Si was selectively removed, leaving

the monocrystalline Si behind, as shown in Fig. 2B.

Example 38

5   Etching was perform d in the same manner as that of Exampl 3 with the xception that a mixture s lution (10:6:50) of buffered hydrofluoric acid (NH₄F: 36.2%, HF 4.5%), thyl alcohol and hydrogen peroxide was used as an etchant. In twelve seconds after initialization of etching, the porous Si was selectively removed with the polycrystalline Si acting as an etch stopper, only the polycrystalline Si and the monocrystalline Si being left behind, as shown in Fig. 3C.

10

Example 39

    Etching was performed in the same manner as that of Example 4 with the exception that a mixture solution (10:6:50) of buffered hydrofluoric acid (NH₄F: 36.2%, HF 4.5%), ethyl alcohol and hydrogen peroxide was used
15 as an etchant. In six seconds after initialization of etching, only the porous Si was selectively removed, leaving the polycrystalline Si and monocrystalline Si behind, as shown in Fig. 4B.

Example 40

20   Etching was performed in the same manner as that of Example 5 with the exception that a mixture solution (10:6:50) of buffered hydrofluoric acid (NH₄F: 36.2%, HF 4.5%), ethyl alcohol and hydrogen peroxide was used as an etchant. In ten minutes after initialization of etching, the porous Si was selectively removed, only the monocrystalline Si being left behind, as shown in Fig. 5C. Finally, the resist was removed (Fig. 5D).

25 Example 41

    Anodization was conducted on a P-type (100) monocrystalline Si substrate having a thickness of 200 µm in a 50% HF solution at a current density of 100 mA/cm². The porous structure formation rate was 8.4 µm/min and hence it took twenty four minutes for the 200 µm-thick P-type (100) Si substrate to be made entirely porous.
30 A Si epitaxial layer with a thickness of of 0.5 µm was grown on the P-type (100) porous Si substrate at a low temperature by molecular beam epitaxy (MBE). Deposition was conducted under the following conditions:
Temperature: 700°C
Pressure: 1 x 10⁻⁹ Torr
Growth rate: 0.1 nm/sec.
35   Next, an optically polished fused silica glass substrate was placed on the surface of the epitaxial layer. The whole structure was then heated at 800°C in an oxygen atmosphere for 0.5 hours to firmly join the two substrates to each other.
    Si₃N₄ was deposited to a thickness of 0.1 µm by plasma CVD method to cover the bonded substrates, and then only the nitride film on the porous substrate was removed by reactive ion etching. Thereafter, selective
40 etching was conducted on the bonded substrates in a 49% hydrofluoric acid solution while the solution was being stirred. In seventy eight minutes, the porous Si substrate was completely etched with the monocrystalline Si layer acting as an etch stopper, only the monocrystalline Si layer being left behind.
    The etching rate of the non-porous monocrystalline Si was so low that only a maximum of 50 Å of non-porous monocrystalline Si was removed in seventy eight minutes. Since the ratio of the etching rate of the non-
45 porous monocrystalline Si to that of the porous layer is 1 : 10⁵ or more, the amount of non-porous layer which is etched (several tens angstroms) can be ignored in a practical operation. That is, the 200 µm-thick porous Si substrate was removed, and subsequently the Si₃N₄ layer was removed with a result that the 0.5 µm-thick monocrystalline Si layer formed on the glass substrate remained.
    The cross-section of the monocrystalline Si layer was observed with a transmission type electron micro-
50 scope. It was found that no crystal defect was newly introduced in the Si layer and hence the Si layer had excellent crystalline structure.

Example 42

55   Anodization was conducted on a P type (100) monocrystalline Si substrate having a thickness of 200 µm in a 50% HF solution at a current density of 100 mA/cm². The porous structure formation rate was 8.4 µm/min and h nce it took twenty four minut s f r the 200 µm-thick P typ (100) Si substrate to be made ntirely porous. A Si pitaxial layer with a thickness of 5.0 µm was grown on the P typ (100) porous Si substrate at a low tem-

p rature by plasma CVD. Depositi n was conducted und r th foll wing conditions:

Gas: SiH_4

High-frequency power: 100 W

Temperatur :   800°C

Pressure: 1×10^{-2} Torr

Growth rat :   2.5 nm/sec.

Next, an optically polished glass substrate having a softening point of about 500 °C was placed on the surface of the epitaxial layer. The whole structure was heated at 450°C in an oxygen atmosphere for 0.5 hours to firmly join the two substrates to each other.

Si_3N_4 was deposited to a thickness of 0.1 μm by plasma CVD to cover the two bonded substrates, and then only the nitride film on the porous substrate was removed by reactive ion etching.

Thereafter, selective etching was conducted on the bonded substrates in a 49% hydrofluoric acid solution while the solution was being stirred. In seventy eight minutes, the porous Si substrate was completely etched with the monocrystalline Si layer acting as an etch stopper, only the monocrystalline Si layer being left behind.

The etching rate of the non-porous monocrystalline Si was so low that only a maximum of 50 Å of non-porous monocrystalline Si was removed in seventy eight minutes. Since the ratio of the etching rate of the non-porous monocrystalline Si to that of the porous layer is $1 : 10^5$ or more, the amount of non-porous layer which is etched (several tens angstroms) can be ignored in a practical operation. That is, the 200 μm-thick porous Si substrate was removed, and subsequently the Si_3N_4 layer was removed with a result that the 5.0 μm-thick monocrystalline Si layer formed on the glass substrate having a low softening point remained.

Example 43

Anodization was conducted on a P type (100) monocrystalline Si substrate having a thickness of 200 μm in a 50% HF solution at a current density of 100 mA/cm². The porous structure formation rate was 8.4 μm/min and hence it took twenty four minutes for the 200 μm-thick P type (100) Si substrate to be made entirely porous. A Si epitaxial layer with a thickness of 1.0 μm was grown on the P type (100) porous Si substrate at a low temperature by bias sputtering. Deposition was conducted under the following conditions:

RF frequency: 100 MHz

High-frequency power: 600 W

Temperature: 300°C

Ar gas pressure: 8×10^{-3} Torr

Growth rate: 120 minutes

Target d.c. bias: -200 V

Substrate d.c. bias: +5 V

Next, an optically polished glass substrate having a softening point of about 500 °C was placed on the surface of the epitaxial layer. The whole structure was heated at 450°C in an oxygen atmosphere for 0.5 hours to firmly join the two substrates to each other.

Si_3N_4 was deposited to a thickness of 0.1 μm by plasma CVD to cover the two bonded substrates, and then only the nitride film on the porous substrate was removed by reactive ion etching.

Thereafter, selective etching was conducted on the bonded substrates in a 49% hydrofluoric acid solution while the solution was being stirred. In seventy eight minutes, the porous Si substrate was completely etched with the monocrystalline Si layer acting as an etch stopper, only the monocrystalline Si layer being left behind.

The etching rate of the non-porous monocrystalline Si was so low that only a maximum of 50 Å of non-porous monocrystalline Si was removed in seventy eight minutes. Since the ratio of the etching rate of the non-porous monocrystalline Si to that of the porous layer is $1 : 10^5$ or more, the amount of non-porous layer which is etched (several tens angstroms) can be ignored in a practical operation. That is, the 200 μm-thick porous Si substrate was removed, and subsequently the Si_3N_4 layer was removed with a result that the 1.0 μm-thick monocrystalline Si layer on the glass substrate having a low softening point remained.

In case of coating of Apiexon Wax or Electron Wax in place of the Si_3N_4 layer, the same effect was obtained and only the Si substrate made porous was completely removed.

Example 44

Anodization was conducted on a N type (100) monocrystalline Si substrate having a thickness of 200 μm in a 50% HF solution at a current density of 100 mA/cm². The porous structure formation rate was 8.4 μm/min and h nce it took twenty four minutes for the 200 μm-thick N type (100) Si substrat to be made ntir ly porous. A Si epitaxial layer with a thickn ss of 10 μm was grown on th N type (100) porous Si substrate at a low tem-

perature by liquid phas growth m thod under the following conditions:

Solvent: Sn, Solute: Si
Growth temperature: 900°C
Growth atmosphere: H_2
Growth time: 20 minut s

Next, an optically polished glass substrate having a soft ning point of about 800 °C was placed n the surface of the epitaxial layer. The whole structure was heated at 750°C in an oxygen atmosphere for 0.5 hours to firmly join the two substrates to each other.

Si_3N_4 was deposited to a thickness of 0.1 μm by plasma CVD to cover the two bonded substrates, and then only the nitride film on the porous substrate was removed by reactive ion etching.

Thereafter, selective etching was conducted on the bonded substrates in a 49% hydrofluoric acid solution while the solution was being stirred. In seventy eight minutes, the porous Si substrate was completely etched with the monocrystalline Si layer acting as an etch stopper, only the monocrystalline Si layer being left behind.

The etching rate of the non-porous monocrystalline Si was so low that only a maximum of 50 Å of non-porous monocrystalline Si was removed in seventy eight minutes. Since the ratio of the etching rate of the non-porous monocrystalline Si to that of the porous layer is 1 : 10^5 or more, the amount of non-porous layer which is etched (several tens angstroms) can be ignored in a practical operation. That is, the 200 μm-thick porous Si substrate was removed, and subsequently the Si_3N_4 layer was removed with a result that the 10 μm-thick monocrystalline Si layer on the glass substrate remained.

Coating of Apiezon Wax in place of the Si_3N_4 layer was also effective and assured complete removal of only the porous Si substrate.

Example 45

Anodization was conducted on a P type (100) monocrystalline Si substrate having a thickness of 200 μm in a 50% HF solution at a current density of 100 mA/cm².

The porous structure formation rate was 8.4 μm/min and hence it took twenty four minutes for the 200 μm-thick P type (100) Si substrate to be made entirely porous. A Si epitaxial layer with a thickness of 1.0 μm was grown on the P type (100) porous Si substrate at a low temperature by low-pressure CVD. Deposition was conducted under the following conditions:

Source gas: SiH_4 800 SCCM
Carrier gas: H_2 150 liter/min
Temperature: 850°C
Pressure: 1 x 10^{-2} Torr
Growth rate: 3.3 nm/sec

Next, an optically polished fuzed silica glass substrate was placed on the surface of the epitaxial layer. The whole structure was heated at 800°C in an oxygen atmosphere for 0.5 hours to firmly join the two substrates to each other.

Si_3N_4 was deposited to a thickness of 0.1 μm by plasma CVD to cover the two bonded substrates, and then only the nitride film on the porous substrate was removed by reactive ion etching.

Thereafter, selective etching was conducted on the bonded substrates in a 49% hydrofluoric acid solution while the solution was being stirred. In seventy eight minutes, the porous Si substrate was completely etched with the monocrystalline Si layer acting as an etch stopper, the monocrystalline Si layer being left behind.

The etching rate of the non-porous monocrystalline Si was so low that only a maximum of 50 Å of non-porous monocrystalline Si was removed in seventy eight minutes. Since the ratio of the etching rate of the non-porous monocrystalline Si to that of the porous layer is 1 : 10^5 or more, the amount of non-porous layer which is etched (several tens angstroms) can be ignored in a practical operation. That is, the 200 μm-thick porous Si substrate was removed, and subsequently the Si_3N_4 layer was removed with a result that the 1.0-thick μm monocrystalline Si layer on the silica glass substrate remained.

When SiH_2Cl_2 was used as the source gas, the growth temperature had to be higher by several tens of degrees. However, high-speed etching characteristics to the porous substrate did not deteriorate.

Example 46

A Si epitaxial layer with a thickness of 1.0 μm was grown on a P type (100) Si substrate having a thickness of 200 μm by CVD. Deposition was conducted under the following conditions:

Reactiv gas flow rate: SiH_4 1000 SCCM
H_2 230 liter/min

Temperature: 1080°C
Pressure: 760 Torr
Time: 2 min

Anodization was conducted on the substrat in a 50% HF solution at a current density of 100 mA/cm². The
porous structure formation rate was 8.4 μm/min and hence it took tw nty four minutes for th 200 μm-thick P
type (100) Si substrat to b made entirely porous. At that tim , there was no chang in the Si epitaxial layer.

Next, an optically polished fuzed silica glass substrate was placed on the surface of the epitaxial layer The
whole structure was heated at 800°C in an oxygen atmosphere for 0.5 hours to firmly join the two substrates
to each other.

Si₃N₄ was deposited to a thickness of 0.1 μm by plasma CVD to cover the two bonded substrates, and
then only the nitride film on the porous substrate was removed by reactive ion etching.

Thereafter, selective etching was conducted on the bonded substrates in a 49% hydrofluoric acid solution
while the solution was being stirred. In seventy eight minutes, the porous Si substrate was completely removed
with the monocrystalline Si layer acting as an etch stopper, only the monocrystalline Si layer being left behind.

The etching rate of the non-porous monocrystalline Si was so low that only a maximum of 50 Å of non-por-
ous monocrystalline Si was removed in seventy eight minutes. Since the ratio of the etching rate of the non-
porous monocrystalline Si to that of the porous layer is 1 : 10⁵, the amount of non-porous layer which is etched
(several tens angstroms) can be ignored in a practical operation. That is, the 200 μm-thick porous Si substrate
was removed, and subsequently the Si₃N₄ layer was removed with a result that the 1.0 μm monocrystalline Si
layer on the silica glass substrate remained.

The cross-section of the monocrystalline Si layer was observed with a transmission type electron micro-
scope. It was found that no crystal defect was newly introduced in the Si layer and hence the Si layer had excel-
lent crystalline structure.

Example 47

A Si epitaxial layer with a thickness of 0.5 μm was grown on a P type (100) Si substrate having a thickness
of 200 μm by CVD. Deposition was conducted under the following conditions:

Reactive gas flow rate: SiH₂Cl₂   1000 SCCM
                            H₂   230 liter/min
Temperature: 1080°C
Pressure: 80 Torr
Time: 1 min

Anodization was conducted on the substrate in a 50% HF solution at a current density of 100 mA/cm². The
porous structure formation rate was 8.4 μm/min and hence it took twenty four minutes for the 200 μm-thick P
type (100) Si substrate to be made entirely porous. As mentioned above, anodization made only the P type
(100) Si substrate porous, and there was no change in the Si epitaxial layer.

Next, an optically polished fuzed silica glass substrate was placed on the surface of the epitaxial layer.
The whole structure was heated at 800°C in an oxygen atmosphere for 0.5 hours to firmly join the two substrates
to each other.

Si₃N₄ was deposited to a thickness of 0.1 μm by plasma CVD to cover the two bonded substrates, and
then only the nitride film on the porous substrate was removed by reactive ion etching.

Thereafter, selective etching was conducted on the bonded substrates in a 49% hydrofluoric acid solution
while the solution was being stirred. In seventy eight minutes, the porous Si substrate was completely etched
with the monocrystalline Si layer acting as an etch stopper, only the monocrystalline Si layer being left behind.

The etching rate of the non-porous monocrystalline Si was so low that only a maximum of 50 Å of non-por-
ous monocrystalline Si was removed in seventy eight minutes. Since the ratio of the etching rate of the non-
porous monocrystalline Si to that of the porous layer is 1 : 10⁵, the amount of non-porous layer which is etched
(several tens angstroms) can be ignored in a practical operation. That is, the 200 μm-thick porous Si substrate
was removed, and subsequently the Si₃N₄ layer was removed with a result that the 0.5 μm-thick monocrystalline
Si layer on the silica glass substrate remained.

The cross-section of the monocrystalline Si layer was observed by a transmission type electron micro-
scope. It was found that no crystal defect was newly introduced in the Si layer and hence the Si layer had excel-
lent crystalline structure.

Example 48

A N typ Si lay r with a thickness of 1 μm was formed on a P type (100) Si substrate having a thickness

of 200 μm by proton implantation. Implantation rate of H⁺ was 5 x 10¹⁵ (ions/cm²).

Anodization was conducted on the substrate in a 50% HF solution at a current density of 100 mA/cm². The porous structure formation rate was 8.4 μm/min and hence it took twenty four minutes for th 200 μm-thick P type (100) Si substrate t b made entirely porous. As mentioned above, anodizati n mad only th P type (100) Si substrat porous, and there was no change in th N typ Si lay r.

Next, an optically polished fuzed silica glass substrat was placed on th surface of the N type Si layer. The whole structure was heated at 800°C in an oxygen atmosphere for 0.5 hours to firmly join the two substrates to each other.

Si_3N_4 was deposited to a thickness of 0.1 μm by plasma CVD to cover the two bonded substrates, and then only the nitride film on the porous substrate was removed by reactive ion etching.

Thereafter, selective etching was conducted on the bonded substrates in a 49% hydrofluoric acid solution while the solution was being stirred. In seventy eight minutes, the porous Si substrate was completely etched with the monocrystalline Si layer acting as an etch stopper, only the monocrystalline Si layer being left behind.

The etching rate of the non-porous monocrystalline Si was so low that only a maximum of 50 Å of non-porous monocrystalline Si was removed in seventy eight minutes. Since the ratio of the etching rate of the non-porous monocrystalline Si to that of the porous layer is 1 : 10⁵, the amount of non-porous layer which is etched (several tens angstroms) can be ignored in a practical operation. That is, the 200 μm-thick porous Si substrate was removed, and subsequently the Si_3N_4 layer was removed with a result that the 1 μm-thick monocrystalline Si layer on the silica glass substrate remained.

The cross-section of the monocrystalline Si layer was observed by a transmission type electron microscope. It was found that no crystal defect was newly introduced in the Si layer and hence the Si layer had excellent crystalline structure.

Example 49

Anodization was conducted on a P type (100) monocrystalline Si substrate having a thickness of 200 μm in a HF solution under the following conditions:

Applied voltage:	2.6 (V)
Current density:	30 (mA·cm⁻²)
Anodizing solution:	$HF:H_2O:C_2H_5OH = 1:1:1$
Time:	1.6 (hour)
Thickness of porous Si:	200 (μm)
Porosity:	56 (%)

A Si epitaxial layer with a thickness of 0.5 μm was grown on the P type (100) porous Si substrate at a low temperature by molecular beam epitaxy (MBE). Deposition was conducted under the following conditions:

Temperature:	700°C
Pressure:	1×10^{-9} Torr
Growth rate:	0.1 nm/sec.

Next, a second Si substrate with a 5000 Å thick oxidized layer formed on the surface thereof was placed on the surface of the epitaxial layer. The whole structure was heated at 800°C in an oxygen atmosphere for 0.5 hours to firmly join the two substrates to each other.

Thereafter, selective etching was conducted on the bonded substrates in a 49% hydrofluoric acid solution while the solution was being stirred. In sixty two minutes, the porous Si substrate was completely etched with the monocrystalline Si layer acting as an etch stopper, only the monocrystalline Si layer being left behind.

The etching rate of the non-porous monocrystalline Si was so low that only a maximum of 50 Å of non-porous monocrystalline Si was removed in sixty-two minutes. Since the ratio of the etching rate of the non-porous monocrystalline Si to that of the porous layer is 1 : 10⁵, the amount of non-porous layer which is etched (several tens angstroms) can be ignored in a practical operation. That is, the 200 μm-thick porous Si substrate was removed with a result that the 0.5 μm-thick monocrystalline Si layer formed on the SiO_2 layer remained.

The cross-section of the monocrystalline Si layer was observed by a transmission type electron microscope. It was found that no crystal defect was newly introduced in the Si layer and hence the Si layer had excellent crystalline structure.

Example 50

Anodization was conducted on a P type (100) monocrystalline Si substrate having a thickness of 200 μm in a HF solution in the same manner as that of Example 49.

A Si epitaxial layer with a thickness of 0.5 μm was gr wn n th P typ (100) porous Si substrate at a low

temperature by plasma CVD. Deposition was c nducted under th following conditions:

Gas: SiH_4
High-frequ ncy power: 100 W
T mperatur :   800°C
Pr ssur : 1×10^{-2} Torr
Growth rate: 2.5 nm/s c.

Next, a second Si substrate with a 5000 Å thick oxidized layer formed on the surface thereof was placed on the surface of the epitaxial layer. The whole structure was heated at 800°C in an oxygen atmosphere for 0.5 hours to firmly join the two substrates to each other.

Thereafter, selective etching was conducted on the bonded substrates in a 49% hydrofluoric acid solution while the solution was being stirred. In sixty two minutes, the porous Si substrate was completely etched with the monocrystalline Si layer acting as an each stopper, only the monocrystalline Si layer being left behind.

The etching rate of the non-porous monocrystalline Si was so low that only a maximum of 50 Å of non-porous monocrystalline Si was removed in sixty-two minutes. Since the ratio of the etching rate of the non-porous monocrystalline Si to that of the porous layer is $1 : 10^5$, the amount of non-porous layer which is etched (several tens angstroms) can be ignored in a practical operation. That is, the 200 μm-thick porous Si substrate was removed with a result that the 0.5 μm thick monocrystalline Si layer on the SiO_2 layer remained.

Example 51

Anodization was conducted on a P type (100) monocrystalline Si substrate having a thickness of 200 μm in a HF solution in the same manner as that of Example 49.

A Si epitaxial layer with a thickness of 0.5 μm was grown on the P type (100) porous Si substrate at a low temperature by bias sputtering. Deposition was conducted under the following conditions:

RF frequency: 100 MHz
High-frequency power: 600 W
Temperature: 300°C
Ar gas pressure: 8×10^{-3} Torr
Growth time: 60 minutes
Target d.c. bias: -200 V
Substrate d.c. bias: +5 V

Next, a second Si substrate with a 5000 Å thick oxidized layer formed on the surface thereof was placed on the surface of the epitaxial layer. The whole structure was heated at 800°C in an oxygen atmosphere for 0.5 hours to firmly join the two substrates to each other.

Thereafter, selective etching was conducted on the bonded substrates in a 49% hydrofluoric acid solution while the solution was being stirred. In sixty two minutes, the porous Si substrate was completely etched with the monocrystalline Si layer acting as an etch stopper, the monocrystalline Si layer being left behind.

The etching rate of the non-porous monocrystalline Si was so low that only a maximum of 50 Å of non-porous monocrystalline Si was removed in sixty-two minutes. Since the ratio of the etching rate of the non-porous monocrystalline Si to that of the porous layer is $1 : 10^5$, the amount of non-porous layer which is etched (several tens angstroms) can be ignored in a practical operation. That is, the 200 μm-thick porous Si substrate was removed with a result that the 0.5 μm thick monocrystalline Si layer on the SiO_2 layer remained.

Example 52

Anodization was conducted on a N type (100) monocrystalline Si substrate having a thickness of 200 μm in a HF solution in the same manner as that of Example 49.

A Si epitaxial layer with a thickness of 5 μm was grown on the N type (100) porous Si substrate at a low temperature by liquid phase growth under the following conditions:

Solvent: Sn,   Solute: Si
Growth temperature: 900°C
Growth atmosphere: H_2
Growth rate: 10 minutes

Next, a second Si substrate with a 5000 Å thick oxidized layer formed on the surface thereof was placed on the surface of the epitaxial layer. The whole structure was heated at 800°C in an oxygen atmosphere for 0.5 hours to firmly join the two substrates to each other.

Th reaft r, s lectiv tching was conduct d n the bonded substrat s in a 49% hydrofluoric acid solution whil the soluti n was being stirred. In sixty two minutes, th porous Si substrate was compl tely etch d with

the monocrystalline Si layer acting as an etch stopper, th monocrystalline Si lay r b ing left b hind.

Th etching rate of the non-porous monocrystallin Si was so low that nly a maximum of 50 Å of non-porous monocrystalline Si was rem ved in sixty-two minutes. Sinc the ratio f th etching rate of the n n-porous monocrystallin Si to that of th porous lay r is 1 : 10⁵, th amount of non-porous layer which is etch d (several tens angstroms) can be ignored in a practical operation. That is, th 200 μm-thick porous Si substrat was removed with a result that th 5 μm thick monocrystalline Si layer on th SiO₂ layer remained.

Example 53

Anodization was conducted on a P type (100) monocrystalline Si substrate having a thickness of 200 μm in a HF solution in the same manner as that of Example 49.

A Si epitaxial layer with a thickness of 1.0 μm was grown on the P type (100) porous Si substrate at a low temperature by low-pressure CVD. Deposition was conducted under the following conditions:

Source gas: SiH₄
Carrier gas: H₂
Temperature: 850°C
Pressure: 1 x 10⁻² Torr
Growth rate: 3.3 nm/sec

Next, a second Si substrate with a 5000 Å thick oxidized layer formed on the surface thereof was placed on the surface of the epitaxial layer. The whole structure was heated at 800°C in an oxygen atmosphere for 0.5 hours to firmly join the two substrates to each other.

Thereafter, selective etching was conducted on the bonded substrates in a 49% hydrofluoric acid solution while the solution was being stirred. In sixty two minutes, the porous Si substrate was completely etched with the monocrystalline Si layer acting as an etch stopper, the monocrystalline Si layer being left behind.

The etching rate of the non-porous monocrystalline Si was so low that only a maximum of 50 Å of non-porous monocrystalline Si was removed in sixty-two minutes. Since the ratio of the etching rate of the non-porous monocrystalline Si to that of the porous layer is 1 : 10⁵, the amount of non-porous layer which is etched (several tens angstroms) can be ignored in a practical operation. That is, the 200 μm-thick porous Si substrate was removed with a result that the 1.0 μm thick monocrystalline Si layer on the SiO₂ layer remained.

When SiH₂Cl₂ was used as the source gas, the growth temperature had to be higher by several tens of degrees. However, high-speed etching characteristics to the porous substrate did not deteriorate.

Example 54

A Si epitaxial layer with a thickness of 1 μm was grown on a P type (100) Si substrate having a thickness of 200 μm by low-pressure CVD. Deposition was conducted under the following conditions:

Reactive gas flow rate: SiH₂Cl₂   1000 SCCM
                              H₂   230 liter/min
Temperature: 1080°C
Pressure: 80 Torr
Time: 2 min

Anodization was conducted on the substrate in a 50% HF solution at a current density of 100 mA/cm². The porous structure formation rate was 8.4 μm/min and hence it took twenty four minutes for the 200 μm-thick P type (100) Si substrate to be made entirely porous. As mentioned above, anodization made only the P type (100) Si substrate porous, and did not affect the Si epitaxial layer at all.

Next, a second Si substrate with a 5000 Å-thick oxidized layer formed on the surface thereof was placed on the surface of the epitaxial layer. The whole structure was heated at 800°C in an oxygen atmosphere for 0.5 hours to firmly join the two substrates to each other.

Thereafter, selective etching was conducted on the bonded substrates in a 49% hydrofluoric acid solution while the solution was being stirred. In sixty two minutes, the porous Si substrate was completely etched with the monocrystalline Si layer acting as an etch stopper, while the monocrystalline Si layer remained.

The etching rate of the non-porous monocrystalline Si was so low that only a maximum of 50 Å of non-porous monocrystalline Si was removed in sixty two minutes. Since the ratio of the etching rate of the non-porous monocrystalline Si to that of the porous layer is 1 : 10⁵, the amount of non-porous layer which is etched (several tens angstroms) can be ignored in a practical operation. That is, the 200 μm-thick porous Si substrate was removed with a result that the 1.0 μm thick monocrystalline Si layer on the SiO₂ layer remained.

The cross-section of the monocrystalline Si layer was observed by a transmission type electron microscope. It was found that no crystal defect was newly introduced in the Si layer and hence the Si layer had excel-

lent crystallin structure.

Example 55

A Si epitaxial lay r with a thickn ss of 5 μm was grown on a P type (100) Si substrate having a thickn ss of 200 μm by atmosph ric CVD. Deposition was conducted under th following conditi ns:

Reactive gas flow rate: SiH_2Cl_2 1000 SCCM

                              H_2 230 liter/min

Temperature: 1080°C

Pressure: 760 Torr

Time: 1 min

Anodization was conducted on the substrate in a HF solution in the same manner as that of Example 49. As mentioned above, anodization made only the P type (100) Si substrate porous, and did not affect the Si epitaxial layer at all.

Next, a second Si substrate with a 5000 Å-thick oxidized layer formed on the surface thereof was placed on the surface of the epitaxial layer. The whole structure was heated at 800°C in an oxygen atmosphere for 0.5 hours to firmly join the two substrates to each other.

Thereafter, selective etching was conducted on the bonded substrates in a 49% hydrofluoric acid solution while the solution was being stirred. In sixty two minutes, the porous Si substrate was completely etched with the monocrystalline Si layer acting as an etch stopper, the monocrystalline Si layer being left behind.

The etching rate of the non-porous monocrystalline Si was so low that only a maximum of 50 Å of non-porous monocrystalline Si was removed in sixty two minutes. Since the ratio of the etching rate of the non-porous monocrystalline Si to that of the porous layer is $1 : 10^5$, the amount of non-porous layer which is etched (several tens angstroms) can be ignored in a practical operation. That is, the 200 μm-thick porous Si substrate was removed with a result that the 5.0 μm thick monocrystalline Si layer on the SiO_2 layer remained.

The cross-section of the monocrystalline Si layer was observed by a transmission type electron microscope. It was found that no crystal defect was newly introduced in the Si layer and hence the Si layer had excellent crystalline structure.

Example 56

A N type Si layer with a thickness of 1 μm was formed on a P type (100) Si substrate having a thickness of 200 μm by proton implantation. Implantation rate of H^+ was 5×10^{15} (ions/cm²).

Anodization was conducted on the substrate in a 50% HF solution at a current density of 100 mA/cm². The porous structure formation rate was 8.4 μm/min and hence it took twenty four minutes for the 200 μm-thick P type (100) Si substrate to be made entirely porous. As mentioned above, anodization made only the P type (100) Si substrate porous, and did not change the N type Si layer.

Next, a second Si substrate with a 5000 Å-thick oxidized layer formed on the surface thereof was placed on the surface of the N type Si layer. The whole structure was heated at 800°C in an oxygen atmosphere for 0.5 hours to firmly join the two substrates to each other.

Thereafter, selective etching was conducted on the bonded substrates in a 49% hydrofluoric acid solution while the solution was being stirred. In sixty two minutes, the porous Si substrate was completely etched with the monocrystalline Si layer acting as an etch stopper, the monocrystalline Si layer being left behind.

The etching rate of the non-porous monocrystalline Si was so low that only a maximum of 50 Å of non-porous monocrystalline Si was removed in sixty two minutes. Since the ratio of the etching rate of the non-porous monocrystalline Si to that of the porous layer is $1 : 10^5$, the amount of non-porous layer which is etched (several tens angstroms) can be ignored in a practical operation. That is, the 200 μm-thick porous Si substrate was removed with a result that the 1.0 μm thick monocrystalline Si layer on the SiO_2 layer remained.

The cross-section of the monocrystalline Si layer was observed by a transmission type electron microscope. It was found that no crystal defect was newly introduced in the Si layer and hence the Si layer had excellent crystalline structure.

Example 57

A P-type (100) single-crystals (monocrystal) Si substrate of a thickness of 200 μ was anodized in 50 % HF solution. The current density then was 100 mA/cm². The porous structure formation rate then was about 8.4 μm/min., and the P-type (100) Si substrate of a thickness of 200 μ was rendered porous in its entirety for 24 minut s.

According to MBE (molecular beam epitaxy) method, an Si epitaxial lay r of 0.5 μ was grown at a lower temperature on th P-typ (100) porous Si substrate. Th conditions for deposition are as follows;

temperature: 700 °C

pressure: 1 x 10⁻⁹ Torr

growth rate: 0.1 nm/sec.

Subsequ ntly, th surfac of th pitaxial lay r was thermally xidized in a depth of 50 nm. A substrat of fused silica glass processed with optical polishing was bonded onto the thermally oxidized membran (i. ., film), and both of the substrates were strongly bonded together by heating at 800 °C for 0.5 hour in oxygen atmosphere.

According to low pressure CVD, Si_3N_4 was deposited to 0.1 μm, thereby coating the bonded two substrates. Thereafter, only the nitride membrane (film) on the porous substrate was removed by reactive ion etching.

Then, the bonded substrates were selectively etched with 49 % hydrofluoric acid. In 78 minutes, only the single-crystal Si layer remained without etching, while the porous Si substrate was selectively etched with the single-crystal Si as a material for etching stopper and then completely removed.

The etching rate of the non-porous Si single-crystal (monocrystal) with the etching solution was extremely low, such as 50 angstroms or less even 78 minutes later, so that the selective ratio of the etching rate of the porous layer to that of the non-porous Si single-crystal was as large as 10^5 or more. The etched amount in the non-porous layer (several tens angstroms) is a practically negligible decrease in membrane thickness. That is, the Si substrate of a thickness of 200 μ, rendered porous, was removed, and after the removal of the Si_3N_4 layer, a single-crystal Si layer of a thickness of 0.5 μm was formed on the substrate of the silica glass.

As a result of observation of the section under a transmission-type electron microscope, it was confirmed that no new crystal defect was introduced in the Si layer and that excellent crystallinity was maintained.

Example 58

A P-type (100) single-crystal Si substrate of a thickness of 200 μ was anodized in 50 % HF solution. The current density then was 100 mA/cm². The porous structure formation rate then was abut 8.4 μm/min., and the P-type (100) Si substrate of a thickness of 200 μ was rendered porous in its entirety for 24 minutes. According to plasma CVD method, an Si epitaxial layer of 5 μ was grown at a lower temperature on the P-type (100) porous Si substrate. The conditions for deposition are as follows;

gas: SiH_4

high-frequency power: 100 W

temperature   800 °C

pressure: 1 x 10⁻² Torr

growth rate: 2.5 nm/sec.

Subsequently, the surface of the epitaxial layer was thermally oxidized in a depth of 50 nm. A glass substrate, having being processed with optical polishing and having a softening point around 500 °C, was bonded onto the thermally oxidized membrane, and both of the substrates were strongly bonded together by heating at 450 °C for 0.5 hour in oxygen atmosphere.

According to plasma CVD method, Si_3N_4 was deposited to 0.1 μm, thereby coating the bonded two substrates. Thereafter, only the nitride membrane on the porous substrate was removed by reactive ion etching.

Then, the bonded substrates were selectively etched with 49 % hydrofluoric acid. In 78 minutes, only the single-crystal Si layer remained without etching, while the porous Si substrate was selectively etched with the single-crystal Si as a material for etching stopper and then completely removed.

The etching rate of the non-porous Si single-crystal with the etching solution was extremely low, such as 50 angstroms or less even 78 minutes later, so that the selective ratio of the ethcing rate of the porous layer to that of the non-porous Si single-crystal was as large as 10^5 or more. The etched amount in the non-porous layer (several tens angstroms) is a practically negligible decrease in membrane thickness. That is, the Si substrate of a thickness of 200 μ, rendered porous, was removed, and after the removal of the Si_3N_4 layer, a single-crystal Si layer of a thickness of 5 μm was formed on the glass substrate of a lower softening point.

Example 59

A P-type (100) single-crystal Si substrate of a thickness of 200 μ was anodized in 50 % HF solution. The current density then was 100 mA/cm². The porous structure formation rate then was abut 8.4 μm/min., and the P-type (100) Si substrate of a thickness of 200 μ was rendered porous in its entirety for 24 minutes. According to thermal CVD method, an Si epitaxial layer of 5 μ was grown at a lower temperature on the P-type (100) porous Si substrate. Th c nditi ns f r dep sition ar as follows;

gas: SiH_4(0.6 l/min), H_2 (100 l/min)
temperature: 850 °C
pressure: 50 Torr
growth rate: 0.1 μm/min.

Subsequntly, th surface of the pitaxial lay r was thermally oxidized in a d pth of 50 nm. A glass substrate, having b ing processed with optical polishing and having a s ftening point around 500 °C, was bonded onto the thermally oxidized membrane, and both of the substrates were strongly bonded tog ther by h ating at 450 °C for 0.5 hour in oxygen atmosphere.

According to plasma CVD method, Si_3N_4 was deposited to 0.1 μm, thereby coating the bonded two substrates. Thereafter, only the nitride membrane on the porous substrate was removed by reactive ion etching.

Then, the bonded substrates were selectively etched with 49 % hydrofluoric acid. In 78 minutes, only the single-crystal Si layer remained without etching, while the porous Si substrate was selectively etched with the single-crystal Si as a material for etching stopper and then completely removed.

The etching rate of the non-porous Si single-crystal with the etching solution was extremely low, such as 50 angstroms or less even 78 minutes later, so that the selective ratio of the etching rate of the porous layer to that of the non-porous Si single-crystal was as large as 10^5 or more. The etched amount in the non-porous layer (several tens angstroms) is a practically negligible decrease in membrane thickness. That is, the Si substrate of a thickness of 200 μ, rendered porous, was removed, and after the removal of the Si_3N_4 layer, a single-crystal Si layer of a thickness of 5 μm was formed on the glass substrate of a lower softening point.

A similar effect could be obtained by using Apiezon wax or electron wax, instead of Si_3N_4, so that only the Si substrate rendered porous could be removed completely.

Example 60

A P-type (100) single-crystal Si substrate of a thickness of 200 μ was anodized in 50 % HF solution. The current density then was 100 mA/cm². The porous structure formation rate then was abut 8.4 μm/min., and the P-type (100) Si substrate of a thickness of 200 μ was rendered porous in its entirety for 24 minutes. According to bias sputter method, an Si epitaxial layer of 1.0 μ was grown at a lower temperature on the P-type (100) porous Si substrate. The conditions for deposition are as follows;

RF frequency: 100 MHz
high-frequency power: 600 W
temperature: 300 °C
Ar gas pressure: 8×10^{-3} Torr
growth time: 120 minutes
target direct current bias: -200 V
substrate direct current bias: +5 V.

Subsequently, the surface of the epitaxial layer was thermally oxidized in a depth of 50 nm. A glass substrate, having being processed with optical polishing and having a softening point around 500 °C, was bonded onto the thermally oxidized membrane, and both of the substrate were strongly bonded together by heating at 450 °C for 0.5 hour in oxygen atmosphere.

According to plasma CVD method, Si_3N_4 was deposited to 0.1 μm, thereby coating the bonded two substrates. Thereafter, only the nitride membrane on the porous substrate was removed by reactive ion etching.

Then, the bonded substrates were selectively etched with 49 % hydrofluoric acid. In 78 minutes, only the single-crystal Si layer remained without etching, while the porous Si substrate was selectively etched with the single-crystal Si as a material for etching stopper and then completely removed.

The etching rate of the non-porous Si single-crystal with the etching solution was extremely low, such as 50 angstroms or less even 78 minutes later, so that the selective ratio of the etching rate of the porous layer to that of the non-porous Si single-crystal was as large as 10^5 or more. The etched amount in the non-porous layer (several tens angstroms) is a practically negligible decrease in membrane thickness. That is, the Si substrate of thickness of 200 μ, rendered porous, was removed, and after the removal of the Si_3N_4 layer, a single-crystal Si layer of a thickness of 1.0 μm was formed on the glass substrate of a lower melting point.

A similar effect could be obtained by using Apiezon wax or electron wax, instead of Si_3N_4, so that only the Si substrate rendered porous could be removed completely.

Example 61

A N-type (100 single-crystal Si substrate of a thickness of 200 μ was anodized in 50 % HF solution. The current d nsity th n was 100 mA/cm². Th porous structure formation rate th n was about 8.4 μm/min., and

the N-typ (100) Si substrate of a thickn ss of 200 μ was rendered porous in its entirety for 24 minutes. Accord-ing to liquid phas growth method, an Si pitaxial layer of 10 μ was grown at a lower t mperature n the N-typ (100) porous Si substrat . The conditions for depositi n are as follows;

solvent: Sn, Solute: Si

growth temp rature: 900°C

growth atmosphere: H$_2$

growth time: 20 minutes.

Subsequently, the surface of the epitaxial layer was thermally oxidized in a depth of 50 nm. A glass sub-strate, having being processed with optical polishing and having a softening point around 800 °C, was bonded onto the thermally oxidized membrane, and both of the substrates were strongly bonded together by heating at 750 °C for 0.5 hour in oxygen atmosphere.

According to low pressure CVD method, Si$_3$N$_4$ was deposited to 0.1 μm, thereby coating the bonded two substrates. Thereafter, only the nitride membrane on the porous substrate was removed by reactive ion etching.

Then, the bonded substrates were selectively etched with 49 % hydrofluoric acid. In 78 minutes, only the single-crystal Si layer remained without etching in 78 minutes, while the porous Si substrate was selectively etched with the single-crystal Si as a material for etching stopper and then completely removed.

The etching rate of the non-porous Si-single crystal with the etching solution was extremely low, such as 50 angstroms or less even 78 minutes later, so that the selective ratio of the etching rate of the porous layer to that of the non-porous Si single-crystal was as large as 10^5 or more. The etched amount in the non-porous layer (several tens angstroms) is a practically negligible decrease in membrane thickness. That is, the Si sub-strate, rendered porous, of a thickness of 200 μ was removed, and after the removal of the Si$_3$N$_4$ layer, a sing-le-crystal Si layer of a thickness of 10 μm was formed on the glass substrate of a lower softening point.

A similar effect could be obtained by using Apiezon wax or electron wax, instead of Si$_3$N$_4$, so that only the Si substrate rendered porous could be removed completely.

Example 62

According to CVD method, an Si epitaxial layer of 0.5 μ was grown at a lower temperature on a P-type (100) Si substrate of a thickness of 200 μ. The conditions for deposition are as follows;

reactive gas flow rate: SiH$_2$Cl$_2$ 1000 SCCM

H$_2$ 230 l/min.

temperature: 1080 °C

pressure: 80 Torr

time: 1 minute.

The present substrate was anodized in 50 % HF solution. The current density then was 100 mA/cm^2. The porous structure formation rate then was about 8,4 μm/min., and the P-type (100) Si substrate of a thickness of 200 μ was rendered porous in its entirety for 24 minutes. As has been described above, the present anodi-zation rendered only the P-type (100) Si substrate porous, but no change was observed in the Si epitaxial layer.

Subsequently, the surface of the epitaxial layer was thermally oxidized in a depth of 50 nm. A substrate of fused silica glass, processed with optical polishing, was bonded onto the thermally oxidized membrane, and both of the substrates were strongly bonded together by heating at 800 °C for 0.5 hour in oxygen atmosphere.

According to low pressure CVD method, Si$_3$N$_4$ was deposited to 0.1 μm, thereby coating the bonded two substrates. Thereafter, only the nitride membrane on the porous substrate was removed by reactive ion etching.

Then, the bonded substrates were selectively etched with 49 % hydrofluoric acid. In 78 minutes, only the single-crystal Si layer remained without etching, while the porous Si substrate was selectively etched with the single-crystal Si as a material for etching stopper and then completely removed.

The etching rate of the non-porous Si single-crystal with the etching solution was extremely low, such as 50 angstroms or less even 78 minutes later, so that the selective ratio of the etching rate of the porous layer to that of the non-porous Si single-crystal was as large as 10^5 or more. The etched amount in the non-porous layer (several tens angstroms) is a practically negligible decrease in membrane thickness. That is, the Si sub-strate of a thickness of 200 μ, rendered porous, was removed, and after the removal of the Si$_3$N$_4$ layer, a sing-le-crystal Si layer of a thickness of 0.5 μm was formed on the glass substrate.

A similar effect could be obtained by using Apiezon wax or electron wax, instead of Si$_3$N$_4$, so that only the Si substrate rendered porous could be removed completely.

As a result of observation of the section under a transmission-type electron microscope, it was confirmed that no new crystal defect was introduced in the Si layer and that excellent crystallinity was maintained.

Example 63

A N-typ Si layer 1 μ was formed on the surface of a P-typ (100) Si substrat of a thickn ss of 200 μ, by

ion implantation of proton. The implanted amount of H⁺ was 5×10^{15} ions/cm². Th substrate was anodized in 50 % HF solution. Th current density then was 100 mA/cm². Th porous structure formation rate th n was about 8.4 μm/min., and the P-typ (100) Si substrate of a thickn ss of 200 μ was rendered porous in its ntirety for 24 minutes. According to the pres nt anodization as has been described abov , nly th P-type (100) Si substrate was rendered porous, but no chang was bserved in the N-type Si layer. Subsequently, th surface of the N-typ single-crystal layer was thermally oxidized in a depth of 50 nm. A substrate of fused silica glass processed with optical polishing was bonded onto th thermally oxidized membran , and both of the substrates were strongly bonded together by heating at 800 °C for 0.5 hour in oxygen atmosphere.

According to low pressure CVD method, Si_3N_4 was deposited to 0.1 μm, thereby coating the bonded two substrates. Thereafter, only the nitride membrane on the porous substrate was removed by reactive ion etching. Then, the bonded substrates were selectively etched with 49 % hydrofluoric acid. In 78 minutes, only the single-crystal Si layer remained without etching, while the porous Si substrate was selectively etched with the single-crystal Si as a material for etching stopper and then completely removed.

The etching rate of the non-porous Si single-crystal with the etching solution was extremely low, such as 50 angstroms or less even 78 minutes later, so that the selective ratio of the etching rate of the porous layer to that of the non-porous Si single-crystal was as large as 10^5 or more. The etched amount in non-porous layer (several tens angstroms) is a practically negligible decrease in membrane thickness. That is, the Si substrate of a thickness of 200 μ, rendered porous, was removed, and after the removal of the Si_3N_4 layer, a single-crystal Si layer of a thickness of 1.0 μm was formed on the glass substrate.

A similar effect could be obtained by using Apiezon wax or electron wax, instead of Si_3N_4, so that only the Si substrate rendered porous could be removed completely.

As a result of observation of the section under a transmission-type electron microscope, it was confirmed that no new crystal defect was introduced in the Si layer and that excellent crystallinity was maintained.

Example 64

A P-type (100) single-crystal Si substrate of a thickness of 200 μ was anodized in 50 % HF solution.
The conditions for deposition are as follows;

applied voltage:	2.6 V
current density:	30 mA-cm⁻²
solution for anodization:	$HF:H_2O:C_2H_5OH = 1:1:1$
time:	1.6 hours
thickness of porous Si:	200 μm
porosity:	56 %.

According to MBE method, an Si epitaxial layer of 0.5 μ was grown at a lower temperature on the P-type (100) porous Si substrate. The conditions for deposition are as follows;

temperature:	700 °C
pressure:	1×10^{-9}
growth rate:	0.1 nm/sec.

Subsequently, an oxidized layer of 1000 angstroms was formed on the surface of the epitaxial layer, and another Si substrate on the surface of which was formed an oxidized layer of 5000 angstroms, was bonded to the oxidized surface. By heating in oxygen atmosphere at 800 °C for 0.5 hour, both of the Si substrates were strongly bonded together.

Then, the bonded substrates were selectively etched with 49 % hydrofluoric acid while under stirring. In 78 minutes, only the single-crystal Si layer remained without etching, while the porous Si substrate was selectively etched with the single-crystal Si as a material for etching stopper and then completely removed.

The etching rate of the non-porous Si single-crystal with the etching solution was extremely low, such as 50 angstroms or less even 78 minutes later, so that the selective ratio of the etching rate of the porous layer to that of the non-porous Si single-crystal was as large as 10^5 or more. The etched amount in the non-porous layer (several tens angstroms) is a practically negligible decrease in membrane thickness. That is, the Si substrate of a thickness of 200 μ, rendered porous, was removed, and after the removal of the Si_3N_4 layer, a single-crystal Si layer of a thickness of 0.5 μm was formed on the SiO_2. As a result of observation of the section under a transmission-type electron microscope, it was confirmed that no new crystal defect was introduced in the Si layer and that excellent crystallinity was maintained.

Example 65

A P-typ (100) single-crystal Si substrate of a thickness of 200 μ was anodized in HF solution.

The conditions for anodization ar as follows;

appli d voltage:	2.6 V
current density:	30 mA.cm^{-2}
solution for anodization:	HF:H$_2$O:C$_2$H$_5$OH = 1:1:1
time:	1.6 hours
thickn ss of porous Si:	200 μm
porosity:	56 %.

According to plasma CVD method, and Si epitaxial layer of 0.5 μ was grown at a lower temperature on the P-type (100) porous Si substrate. The conditions for deposition are as follows;

gas:	SiH$_4$
high-frequency power:	100 W
temperature:	800 °C
pressure:	1 x 10^{-2} Torr
growth rate:	2.5 nm/sec.

Subsequently, an oxidized layer of 1000 angstroms was formed on the surface of the epitaxial layer, and another Si substrate on the surface of which was formed as oxidized layer of 5000 angstroms was bonded to the oxidized surface. By heating in oxygen atmosphere at 800 °C for 0.5 hour, both of the Si substrates were strongly bonded together.

Then, the bonded substrates were selectively etched with 49 % hydrofluoric acid while under stirring. In 78 minutes, only the single-crystal Si layer remained without etching, while the porous Si substrate was selectively etched with the single-crystal Si as a material for etching stopper and then completely removed.

The etching rate of the non-porous Si single-crystal with the etching solution was extremely low, such as 50 angstroms or less even 78 minutes later, so that the selective ratio of the etching rate of the porous layer to that of the non-porous Si single-crystal was as large as 10^5 or more. The etched amount in the non-porous layer (several tens angstroms) is a practically negligible decrease in membrane thickness. That is, the Si substrate of a thickness of 200 μ, rendered porous, was removed, and a single-crystal Si layer of a thickness of 0.5 μm was formed on the SiO$_2$.

Example 66

A P-type (100) single-crystal Si substrate of a thickness of 200 μ was anodized in HF solution.

The conditions for anodization are as follows;

applied voltage:	2.6 V
current density:	30 mA.cm^{-2}
solution for anodization:	HF:H$_2$O:C$_2$H$_5$OH = 1:1:1
time:	1.6 hours
thickness of porous Si:	200 μm
porosity:	56 %.

According to bias sputter method, an Si epitaxial layer of 0.5 μ was grown at a lower temperature on the P-type (100) porous Si substrate. The conditions for deposition are as follows;

RF frequency:	100 MHz
high-frequency power:	600 W
temperature:	300 °C
Ar gas pressure:	8 x 10^{-3} Torr
growth time:	60 minutes
target direct current bias:	-200 V
substrate direct current bias:	+5 V.

Subsequently, an oxidized layer of 1000 angstroms was formed on the surface of the epitaxial layer, and another Si substrate on the surface of which was formed an oxidized layer of 5000 angstroms was bonded to the oxidized surface. By heating in oxygen atmosphere at 800 °C for 0.5 hour, both of the Si substrates were strongly bonded together.

Then, the bonded substrates were selectively etched with 49 % hydrofluoric acis while under stirring. In 78 minutes, only the single-crystal Si layer remained without etching, while the porous Si substrate was selectively etched with the single-crystal Si as a material for etching stopper and then completely removed. The etching rate of the non-porous Si single-crystal with the etching solution was extremely low, such as 50 angstroms or less even 78 minutes later, so that the selective ratio of the etching rate of the porous layer to that of the non-porous Si single-crystal was as large as 10^5 or more. The etched amount in the non-porous layer (several tens angstroms) is a practically n gligible d crease in m mbrane thickness. That is, the Si substrate of a thick-

ness of 200 µ, r nder d porous, was removed, and a single-crystal Si layer of a thickness of 0.5 µm was formed on the SiO$_2$.

Exampl 67

A N-typ (100) single-crystal Si substrat of a thickn ss of 200 µ was anodized in HF solution.
Th conditions for anodization ar as follows;

applied voltage:	2.6 V
current density:	30 mA.cm^{-2}
solution for anodization:	HF:H$_2$O:C$_2$H$_5$OH = 1:1:1
time:	1.6 hours
thickness of porous Si:	200 µm
porosity:	56 %.

According to liquid phase growth method, an Si epitaxial layer of 5 µ was grown at a lower temperature on the N-type (100) porous Si substrate. The conditions for growth are as follows;

solvent:	Sn,	Solute:	Si
growth temperature:	900°C		
growth atmosphere:	H$_2$		
growth period:	10 minutes		

Subsequently, an oxidized layer of 1000 angstroms was formed on the surface of the epitaxial layer, and another Si substrate on the surface of which was formed an oxidized layer of 5000 angstroms was bonded to the oxidized surface. By heating in oxygen atmosphere at 800 °C for 0.5 hour, both of the Si substrates were strongly bonded together.

Then, the bonded substrates were selectively etched with 49 % hydrofluoric acid while under stirring. Only the single-crystal Si layer remained without etching in 78 minutes, while the porous Si substrate was selectively etched with the single-crystal Si as a material for etching stopper and then completely removed.

The etching rate of the non-porous Si single-crystal with the etching solution was extremely low, such as 50 angstroms or less even 78 minutes layer, so that the selective ratio of the etching rate of the porous layer to that of the non-porous Si single-crystal was as large as 10^5 or more. The etched amount in the non-porous layer (several tens angstroms) is a practically negligible decrease in membrane thickness. That is, the Si substrate of a thickness of 200 µ, rendered porous, was removed, and a single-crystal Si layer of a thickness of 0.5 µm was formed on the SiO$_2$.

Example 68

A P-type (100) single-crystal Si substrate of a thickness of 200 µ was anodized in HF solution.
The conditions for anodization are as follows;

applied voltage:	2.6 V
current density:	30 mA-cm^{-2}
solution for anodization:	HF:H$_2$O:C$_2$H$_5$OH = 1:1:1
time:	1.6 hours
thickness of porous Si:	200 µm
porosity:	56 %.

According to low pressure CVD method, an Si epitaxial layer of 1.0 µ was grown at a lower temperature on the P-type (100) porous Si substrate. The conditions for deposition are as follows;

source gas:	SiH$_4$
carrier gas:	H$_2$
temperature:	850 °C
pressure:	1 x 10^{-2} Torr
growth rate:	3.3 nm/sec.

Subsequently, an oxidized layer of 1000 angstroms was formed on the surface of the epitaxial layer, and another Si substrate on the surface of which was formed an oxidized layer of 5000 angstroms was bonded to the oxidized surface. By heating in oxygen atmosphere at 800 °C for 0.5 hour, both of the Si substrates were strongly bonded together.

Then, the bonded substrates were selectively etched with 49 % hydrofluoric acid while under stirring. In 78 minutes, only the single-crystal Si layer remained without etching in 78 minutes, while the porous Si substrate was selectively etched with the single-crystal Si as a material for etching stopper and then completely removed.

Th etching rat of the non-por us Si single-crystal with the etching solution was extremely low, such as

50 angstroms or l ss ev n 78 minut s later, so that the selectiv ratio of the tching rat of th porous layer to that of th non-porous Si single-crystal was as larg as 10⁵ or more. The tch d amount in th non-porous layer (several t ns angstroms) is a practically n gligibl decreas in m mbrane thickn ss. That is, th Si substrate, r nd red porous, of a thickness of 200 μ was r mov d, and a single-crystal Si layer of a thickness of 1.0 μm was formed on the SiO₂. When SiH₂Cl₂ was used a a source gas, it was required to rai e th growth temperature by sev ral tens of degrees. N v rthel ss, th accelerating tching characteristics to porous substrates was maintained.

Example 69

According to low pressure CVD method, an Si epitaxial layer of 1 μ was grown at a lower temperature on a P-type (100) porous Si substrate. The conditions for deposition are as follows;

reactive gas flow rate:	SiH₂Cl₂	1000 SCCM
	H₂	230 l/min
temperature:	1080 °C	
pressure:	80 Torr	
time:	2 min.	

The substrate was anodized in 50 % HF solution. The current density then was 100 mA/cm². The porous structure formation rate then was 8.4 μm/min., and the P-type (100) Si substrate of a thickness of 200 μ was rendered porous in its entirety for 24 minutes. According to the present anodization, as has been described above, only the P-type (100) Si substrate was rendered porous, but no change was observed in the Si epitaxial layer.

Subsequently, an oxidized layer of 1000 angstroms was formed on the surface of the epitaxial layer, and another Si substrate on the surface of which was formed an oxidized layer of 5000 angstroms was bonded to the oxidized surface. By heating in oxygen atmosphere at 800 °C for 0.5 hour, both of the Si substrates were strongly bonded together.

Then, the bonded substrates were selectively etched with 49 % hydrofluoric acid while under stirring. In 78 minutes, only the single-crystal Si layer remained without etching, while the porous Si substrate was selectively etched with the single-crystal Si as a material for etching stopper and then completely removed.

The etching rate of the non-porous Si single-crystal with the etching solution was extremely low, such as 50 angstroms or less even 78 minutes later, so that the selective ratio of the etching rate of the porous layer to that of the non-porous Si single-crystal was as large as 10⁵ or more. The etched amount in the non-porous layer (several tens angstroms) is a practically negligible decrease in membrane thickness. That is, the Si substrate of a thickness of 200 μ, rendered porous, was removed, and a single-crystal Si layer of a thickness of 1.0 μm was formed on the SiO₂.

As a result of observation of the section under a transmission-type electron microscope, it was confirmed that no new crystal defect was introduced in the Si layer and that excellent crystallinity was maintained.

Example 70

According to atmospheric pressure CVD method, an Si epitaxial layer of 5 μ was grown at a lower temperature on a P-type (100) Si substrate. The conditions for deposition are as follows;

reactive gas flow rate:	SiH₂Cl₂	1000 SCCM
	H₂	230 l/min
temperature:	1080 °C	
pressure:	760 Torr	
time:	1 min.	

The Si substrate was anodized in HF solution.
The conditions for anodization are as follows;

applied voltage:	2.6 V
current density:	30 mA-cm⁻²
solution for anodization:	HF:H₂O:C₂H₅OH = 1:1:1
time:	1.6 hours
thickness of porous Si:	200 μm
porosity:	56 %.

According to the present anodization as has been described above, only the P-type (100) Si substrate was rendered porous, but no change was observed in the Si epitaxial layer.

Subsequently, an oxidized layer of 1000 angstroms was formed on the surface f the epitaxial layer, and

another Si substrate on the surface of which was formed an xidiz d layer of 5000 angstroms was bond d to the oxidiz d surface. By heating in xygen atmosph r at 800 °C for 0.5 hour, both f th Si substrates w re strongly bond d tog th r.

Th n, th bonded substrates were selectively etched with 49 % hydrofluoric acid whil und r stirring. In 78 minutes, nly th single-crystal Si layer remained without tching, whil th porous Si substrat was selectively etch d with the single-crystal Si as a material for tching stopper and th n compl tely removed.

Th etching rat of the non-porous Si single-crystal with th tching solution was extremely low, such as 50 angstroms or less even 78 minutes later, so that the selective ratio of the etching rate of the porous layer to that of the non-porous Si single-crystal was as large as 10^5 or more. The etched amount in the non-porous layer (several tens angstroms) is a practically negligible decrease in membrane thickness. That is, the Si substrate, rendered porous, of a thickness of 200 μ was removed, and a single-crystal Si layer of a thickness of 5 μm was formed on the SiO_2. As a result of observation of the section under a transmission-type electron microscope, it was confirmed that no new crystal defect was introduced in the Si layer and that excellent crystallinity was maintained.

Example 71

A N-type Si layer of 1 μ was formed on the surface of a P-type (100) Si substrate of a thickness of 200 μ, by ion implantation of proton. The implanted amount of H^+ was 5 x 10^{15} ions/cm^2. The substrate was anodized in 50 % HF solution. The current density then was 100 mA/cm^2. The porous structure formation rate then was 8.4 μm/min., and the P-type (100) Si substrate of a thickness of 200 μ was rendered porous in its entirety for 24 minutes. According to the present anodization as has been described above, only the P-type (100) Si substrate was rendered porous, but no change was observed in the N-type Si layer.

Subsequently, an oxidized layer of 1000 angstroms was formed on the surface of the N-type Si layer, and another Si substrate on the surface of which was formed an oxidized layer of 5000 angstroms was bonded to the oxidized surface. By heating in oxygen atmosphere at 800 °C for 0.5 hour, both of the Si substrates were strongly bonded together.

Then, the bonded substrates were selectively etched with 49 % hydrofluoric acid with stirring. In 78 minutes, only the single-crystal Si layer remained without etching, while the porous Si substrate was selectively etched with the single-crystal Si as a material for etching stopper and then completely removed.

The etching rate of the non-porous Si single-crystal with the etching solution was extremely low, such as 50 angstroms or less even 78 minutes later, so that the selective ratio of the etching rate of the porous layer to that of the non-porous Si single-crystal was as large as 10^5 or more. The etched amount in the non-porous layer (several tens angstroms) is a practically negligible decrease in membrane thickness. That is, the Si substrate, rendered porous, of a thickness of 200 μ was removed, and a single-crystal Si layer of a thickness of 1.0 μm was formed on SiO_2.

As a result of observation of the section under a transmission-type electron microscope, it was confirmed that no new crystal defect was introduced in the Si layer and that excellent crystallinity was maintained.

Example 72

A P-type (100) single-crystal Si substrate of a thickness of 200 μ was anodized in 50 % HF solution. The current density then was 100 mA/cm^2. The porous structure formation rate then was about 8.4 μm/min., and the P-type (100) Si substrate of a thickness of 200 μ was rendered porous in its entirety for 24 minutes.

According to MBE (monocular beam epitaxy) method, an Si epitaxial layer was grown at a lower temperature on the P-type (100) porous Si substrate. The conditions for deposition are as follows;
temperature: 700 °C
pressure: 1 x 10^{-9} Torr
growth rate: 0.1 nm/sec.

Subsequently, a substrate of fused silica glass processed with optical polishing was bonded onto the the surface of the epitaxial layer, and both of the substrates were strongly bonded together by heating at 800 °C for 0.5 hour in oxygen atmosphere.

According to plasma CVD method, Si_3N_4 was deposited to 0.1 μm, thereby coating the bonded two substrates. Thereafter, only the nitride membrane on the porous substrate was removed by reactive ion etching. Then, the bonded substrates were selectively etching with a mixed solution of 49 % hydrofluoric acid and alcohol (10:1), without stirring. In 82 minutes, only the single-crystal Si layer remained without etching, while the porous Si substrate was selectively etched with the single-crystal Si as a material for etching stopper, and completely remov d.

The etching rate of th non-porous Si single-crystal with th etching solution was extremely low, such as 50 angstroms or less ven 82 minutes lat r, so that the selectiv ratio of th etching rate of th porou layer to that of th non-porous Si single-crystal was as large as 10^5 or more. Th etch d amount in the non-porous layer (sev ral tens angstroms) is a practically negligible decreas in m mbrane thickn ss. That is, th Si substrate of a thickness of 200 μ, rendered porous, was r mov d, and after th removal of the Si_3N_4 lay r, a single-crystal Si lay r of a thickn ss of 0.5 μm was formed on the substrat of the glass.

As a result of observation of the section under a transmission-type electron microscope, it was confirmed that no new crystal defect was introduced in the Si layer and that excellent crystallinity was maintained.

Examples 73 to 86

The same procedure as in Examples 42 to 55 was effected, replacing the etching solution used in Examples 42 to 55 with that in Example 72. In any of the present Examples, consequently, a single-crystal Si layer was formed with extremely less crystal defect on insulating materials.

Example 87

A N-type Si layer of 1 μ was formed on the surface of a P-type (100) Si substrate of a thickness of 200 μ, by ion implantation of proton. The implanted amount of H^+ was 5×10^{15} ions/cm^2.

The substrate was anodized in 50 % HF solution. The current density then was 100 mA/cm^2. The porous structure formation rate then was 8.4μm/min., and the P-type (100) Si substrate of a thickness of 200 μ was rendered porous in its entirety for 24 minutes. According to the present anodization as has been described above, only the P-type (100) Si substrate was rendered porous, but no change was observed in the N-type Si layer.

Subsequently, a second Si substrate on the surface of which was formed an oxidized layer of 5000 angstroms, was bonded to the surface of the N-type Si layer. By heating in oxygen atmosphere at 800 °C for 0.5 hour, both of the Si substrates were strongly bonded together.

Then, the bonded substrates were selectively etched with a mixed solution of 49 % hydrofluoric acid and alcohol (10:1) without stirring. In 82 minutes, only the single-crystal Si layer remained without etching, while the porous Si substrate was selectively etched with the single-crystal Si as a material for etching stopper and then completely removed.

The etching rate of the non-porous Si single-crystal with the etching solution was extremely low, such as 50 angstroms or less even 82 minutes later, so that the selective ratio of the etching rate of the porous layer to that of the non-porous Si single-crystal was as large as 10^5 or more. The etched amount in the non-porous layer (several tens angstroms) is a practically negligible decrease in membrane thickness. That is, the Si substrate of a thickness of 200 μ, rendered porous, was removed, and a single-crystal Si layer of a thickness of 1.0 μm was formed on the SiO_2 layer.

As a result of observation of the section under a transmission-type electron microscope, it was confirmed that no new crystal defect was introduced in the Si layer and that excellent crystallinity was maintained.

Examples 88 to 102

The same procedure as in Examples 57 to 71 was effected, replacing the etching solution in Examples 57 to 71 with that in Example 72. In any of the present Examples, consequently, a single-crystal Si layer was formed with extremely less crystal defect on insulating materials.

Example 103

A P-type (100) single-crystal Si substrate of a thickness of 200 μ was anodized in 50 % HF solution. The current density then was 100 mA/cm^2. The porous structure formation rate then was about 8.4 μm/min., and the P-type (100) Si substrate of a thickness of 200 μ was rendered porous in its entirety for 24 minutes.

According to MBE (molecular beam epitaxy) method, an Si epitaxial layer of 0.5 μ was grown at a lower temperature on the P-type (100) porous Si substrate. The conditions for deposition are as follows;

temperature: 700 °C
pressure: 1×10^{-9} Torr
growth rate: 0.1 nm/sec.

Subsequently, a substrate of fused silica glass processed with optical polishing was bonded onto the surface of th pitaxial layer, and both of the substrates were strongly bond d together by heating at 800 °C for

0.5 hour in oxygen atmosph re.

According to plasma CVD method, Si_3N_4 was deposited at 0.1 μm, th r by coating th bonded two subs-trates. Th reaft r, nly th nitrid membran on th porous substrate was removed by reactiv ion tching. Then, the bonded substrates were selectively tch d with a mixed solution of 49 % hydrofluoric acid and aqueous hydrog n peroxid solution (1:5), while under stirring. In 62 minutes, only the single-crystal Si layer remain d without tching, whl the porous Si substrate was s l ctiv ly etched with th single-crystal Si as a material for etching stopper and completely removed.

The etching rate of the non-porous Si single-crystal with the etching solution was extremely low, such as 50 angstroms or less even 62 minutes later, so that the selective ratio of the etching rate of the porous layer to that of the non-porous Si single-crystal was as large as 10^5 or more. The etched amount in the non-porous layer (several tens angstroms) is a practically negligible decrease in membrane thickness. That is, the Si sub-strate of a thickness of 200 μ, rendered porous, was removed, and after the removal of the Si_3N_4 layer, a sing-le-crystal Si layer of a thickness of 0.5 μm was formed on the substrate of the glass.

As a result of observation of the section under a transmission-type electron microscope, it was confirmed that no new crystal defect was introduced in the Si layer and that excellent crystallinity was maintained.

Examples 104 to 118

The same procedure as in Examples 42 to 56 was effected, replacing the etching solution in Examples 42 to 56 with that in Example 103. In any of the present Examples, consequently, a single-crystal Si layer was formed with extremely less crystal defect on insulating materials.

Example 119

A P-type (100) single-crystal Si substrate of a thickness of 200 μ was anodized in 50 % HF solution. The current density then was 100 mA/cm². The porous structure formation rate then was about 8.4 μm/min., and the P-type (100) Si substrate of a thickness of 200 μ was rendered porous in its entirety for 24 minutes.

According to MBE (molecular beam epitaxy) method, an Si epitaxial layer of 0.5 μ was grown at a lower temperature on the P-type (100) porous Si substrate. The conditions for deposition are as follows;

temperature: 700 °C
pressure: 1×10^9 Torr
growth rate: 0.1 nm/sec.

Subsequently, the surface of the epitaxial layer was thermally oxidized in a depth of 50 nm. A substrate of fused silica glass processed with optical polishing was bonded onto the thermally oxidized membrane, and both of the substrates were strongly bonded together by heating at 800 °C for 0.5 hour in oxygen atmosphere.

According to low pressure CVD method, Si_3N_4 was deposited to 0,1 μm, thereby coating the bonded two substrates. Thereafter, only the nitride membrane on the porous substrate was removed by reactive ion etching.

Then, the bonded substrates were selectively etched with a mixed solution of 49 % hydrofluoric acid and aqueous hydrogen peroxide solution (1:5). In 62 minutes, only the single-crystal Si layer remained without etch-ing, while the porous Si substrate was selectively etched with the single-crystal Si as a material for etching stop-per and completely removed.

The etching rate of the non-porous Si single-crystal with the etching solution was extremely low, such as 50 angstroms or less even 62 minutes later, so that the selective ratio of the etching rate of the porous layer to that of the non-porous Si single-crystal was as large as 10^5 or more. The etched amount in the non-porous layer (several tens angstroms) is a practically negligible decrease in membrane thickness. That is, the Si sub-strate of a thickness of 200 μ, rendered porous, was removed, and after the removal of the Si_3N_4 layer, a sing-le-crystal Si layer of a thickness of 0.5 μm was formed on the substrate of the silica glass.

As a result of observation of the section under a transmission-type electron microscope, it was confirmed that no new crystal defect was introduced in the Si layer and that excellent crystallinity was maintained.

Examples 120 to 133

The same procedure as in Examples 58 to 71 was effected, replacing the etching solution in Examples 58 to 71 with that in Example 103. In any of the present Examples, consequently, a single-crystal Si layer was formed with extremely less crystal defect on insulating materials.

Example 134

A P-typ (100) single-crystal Si substrate of a thickness of 200 μ was anodized in 50 % HF solution. Th curr nt d nsity then was 100 mA/cm². Th porous structure formation rat th n was 8.4 μm/min., and th P-type (100) Si substrat of a thickness of 200 μ was rendered porous in its ntirety for 24 minutes.

According to MBE (mol cular b am pitaxy) method, an Si epitaxial layer of 0.5 μ was grown at a lower temperature on th P-type (100) porous Si substrate. Th conditions for d position are as follows;

temperature: 700 °C
pressure: 1 x 10⁻⁹ Torr
growth rate: 0.1 nm/sec.

Subsequently, a substrate of fused silica glass processed with optical polishing was bonded onto the surface of the epitaxial layer, and both of the substrates were strongly bonded together by heating at 800 °C for 0.5 hour in oxygen atmosphere.

According to plasma CVD method, Si_3N_4 was deposited to 0.1 μm, thereby coating the bonded two substrates. Thereafter, only the nitride membrane on the porous substrate was removed by reactive ion etching. Then, the bonded substrates were selectively etched with a mixed solution of 49 % hydrofluoric acid, alcohol and aqueous hydrogen peroxide solution (10:6:50), without stirring. In 65 minutes, only the single-crystal Si layer remained without etching, while the porous Si substrate was selectively etched with the single-crystal Si as a material for etching stopper and completely removed.

The etching rate of the non-porous Si single crystal with the etching solution was extremely low, such as approximately slightly less than 40 angstroms even 65 minutes later, so that the selective ratio of the etching rate of the porous layer to that of the non-porous Si single-crystal was as large as 10^5 or more. The etched amount in the non-porous layer (several tens angstroms) is a practically negligible decrease in membrane thickness. That is, the Si substrate of a thickness of 200 μ, rendered porous, was removed, and after the removal of the Si_3N_4 layer, a single-crystal Si layer of a thickness of 0.5 μm was formed on the substrate of the silica glass.

As a result of observation of the section under a transmission-type electron microscope, it was confirmed that no new crystal defect was introduced in the Si layer and that excellent crystallinity was maintained.

Examples 135 to 148

The same procedure as in Examples 42 to 55 was effected, replacing the etching solution in Examples 42 to 55 with that in Example 134. In any of the present Examples, consequently, a single-crystal Si layer was formed with extremely less crystal defect on insulating materials.

Example 149

A N-type Si layer of 1 μ was formed on the surface of a P-type (100) Si substrate of a thickness of 200 μ, by ion implantation of proton. The implanted amount of H⁺ was 5 x 10¹⁵ ions/cm².

The substrate was anodized in 50 % HF solution. The current density then was 100 mA/cm². The porous structure formation rate then was 8.4 μm/min., and the P-type (100) Si substrate of a thickness of 200 μ was rendered porous in its entirety for 24 minutes. According to the present anodization as has been described above, only the P-type (100) Si substrate was rendered porous, but no change was observed in the N-type Si layer.

Subsequently, a second Si substrate on the surface of which was formed an oxidized layer of 5000 angstroms was bonded to the surface of the N-type Si layer. By heating in oxygen atmosphere at 800 °C for 0.5 hour, both of the substrates were strongly bonded together.

Then, the bonded substrates were selectively etched with a mixed solution of 49 % hydrofluoric acid, alcohol and aqueous 30 % hydrogen peroxide solution (10:6:50) without stirring. In 65 minutes, only the single-crystal Si layer remained without etching, while the porous Si substrate was selectively etched with the single-crystal Si as a material for etching stopper, and then completely removed.

The etching rate of the non-porous Si single-crystal with the etching solution was extremely low, such as 50 angstroms or less even 65 minutes later, so that the selective ratio of the etching rate of the porous layer to that of the non-porous Si single-crystal was as large as 10^5 or more. The etched amount in the non-porous layer (several tens angstroms) is a practically negligible decrease in membrane thickness. That is, the Si substrate of a thickness of 200 μ, rendered porous, was removed, and a single-crystal Si layer of a thickness of 1.0 μm was formed on the SiO_2 layer.

As a result of observation of th section und r a transmission-type l ctron microscop , it was confirmed

that no new crystal defect was introduced in the Si layer and that excell nt crystallinity was maintained.

Examples 150 to 164

5   Th same procedure as in Exampl s 57 to 71 was effected, replacing th tching solution in Examples 57 to 71 with that in Exampl 134. In any of th pr sent Exampl s, consequ ntly, a single-crystal Si lay r was formed with extremely less crystal defect on insulating materials.

Example 165

10

A P-type (100) single-crystal Si substrate of a thickness of 200 μ was anodized in 50 % HF solution. The current density then was 100 mA/cm². The porous structure formation rate then was 8.4 μm/min., and the P-type (100) Si substrate of a thickness of 200 μ was rendered porous in its entirety for 24 minutes.

According to MBE (molecular beam epitaxy) method, an Si epitaxial layer of 0.5 μ was grown at a lower
15   temperature on the P-type (100) porous Si substrate. The conditions for deposition are as follows;

temperature: 700 °C

pressure: 1 x 10⁻⁹ Torr

growth rate: 0.1 nm/sec.

Subsequently, a substrate of fused silica glass processed with optical polishing was bonded onto the sur-
20   face of the epitaxial layer, and both of the substrates were strongly bonded together by heating at 800 °C for 0.5 hour in oxygen atmosphere.

According to plasma CVD method, Si_3N_4 was deposited to 0.1 μm, thereby coating the bonded two substrates. Thereafter, only the nitride membrane on the porous substrate was removed by reactive ion etching. Then, the bonded substrates were selectively etched, under stirring, with buffered hydrofluoric acid. In 258
25   minutes, only the single-crystal Si layer remained without etching, while the porous Si substrate was selectively etched with the single-crystal Si as a material for etching stopper and then completely removed.

The etching rate of the non-porous Si single-crystal with the etching solution was extremely low, such as 100 angstroms or less even 258 minutes later, so that the selective ratio of the etching rate of the porous layer to that of the non-porous Si single-crystal was as large as 10⁵ or more. The etched amount in the non-porous
30   layer (several tens angstroms) is a practically negligible decrease in membrane thickness. That is, the Si substrate of a thickness of 200 μ, rendered porous, was removed, and after the removal of the Si_3N_4 layer, a single-crystal Si layer of a thickness of 0.5 μm was formed on the substrate of the glass.

As a result of observation of the section under a transmission-type electron microscope, it was confirmed that no new crystal defect was introduced in the Si layer and that excellent crystallinity was maintained.

35

Examples 166 to 180

The same procedure as in Examples 42 to 56 was effected, replacing the etching solution in Examples 42 to 56 with that in Example 165. In any of the present Examples, consequently, a single-crystal Si layer was
40   formed with extremely less crystal defect on insulating materials.

Example 181

A P-type (100) single-crystal Si substrate of a thickness of 200 μ was anodized in 50 % HF solution. The
45   current density then was 100 mA/cm². The porous structure formation rate then was about 8.4 μm/min., and the P-type (100) Si substrate of a thickness of 200 μ was rendered porous in its entirety for 24 minutes.

According to MBE (molecular beam epitaxy) method, an Si epitaxial layer of 0.5 μ was grown at a lower temperature on the P-type (100) porous Si substrate. The conditions for deposition are as follows;

temperature: 700 °C

50   pressure: 1 x 10⁻⁹ Torr

growth rate: 0.1 nm/sec.

Subsequently, the surface of the epitaxial layer was thermally oxidized in a depth of 50 nm. A substrate of fused silica glass processed with optical polishing was bonded onto the thermally oxidized membrane, and both of the substrates were strongly bonded together by heating at 800 °C for 0.5 hour in oxygen atmosphere.

55   According to low pressure CVD method, Si_3N_4 was deposited to 0.1 μm, thereby coating the bonded two substrates. Thereafter, only the nitride membrane on the porous substrate was removed by reactive ion etching.

Then, the bonded substrates were immersed in buffered hydrofluoric acid, and stirred. In 258 minutes, only the single-crystal Si layer remained without etching, while the porous Si substrates was selectively etched with

the single-crystal Si as a material for etching stopp r and then completely removed.

Th tching rate of the non-porous Si ingle-crystal with th tching solution was extremely low, such as 100 angstroms or less ven 258 minutes later, so that th selective ratio of th etching rat of the porous layer to that of the n n-porous Si single-crystal was as larg as 10⁵ or more. The tched amount in th non-porous layer (several t ns angstroms) is a practically negligibl decrease in m mbran thickn ss. That is, th Si substrate of a thickness of 200 μ, rendered porous, was removed, and aft r the removal of the Si₃N₄ lay r, a sing-l -crystal Si layer of a thickn ss of 0.5 μm n th substrate of the silica glass was formed.

As a result of observation of the section under a transmission-type electron microscope, it was confirmed that no new crystal defect was introduced in the Si layer and that excellent crystallinity was maintained.

Examples 182 to 195

The same procedure as in Examples 58 to 71 was effected, replacing the etching solution in Examples 58 to 71 with that in Example 165. In any of the present Examples, consequently, a single-crystal Si layer was formed with extremely less crystal defect on insulating materials.

Example 196

A P-type (100) single-crystal Si substrate of a thickness of 200 μ was anodized in 50 % HF solution. The current density then was 100 mA/cm². The porous structure formation rate then was 8.4 μm/min., and the P-type (100) Si substrate of a thickness of 200 μ was rendered porous in its entirety for 24 minutes.

According to MBE (molecular beam epitaxy) method, an Si epitaxial layer of 0.5 μ was grown at a lower temperature on the P-type (100) porous Si substrate. The conditions for deposition are as follows;

temperature: 700 °C
pressure: 1 x 10⁻⁹ Torr
growth rate: 0.1 nm/sec.

Subsequently, a substrate of fused silica glass processed with optical polishing was bonded onto the surface of the epitaxial layer, and both of the substrates were strongly bonded together by heating at 800 °C for 0.5 hour in oxygen atmosphere.

According to plasma CVD method, Si₃N₄ was deposited to 0.1 μm, thereby coating the bonded two substrates. Thereafter, only the nitride membrane on the porous substrate was removed by reactive ion etching. Then, the bonded substrates were selectively etched in a mixed solution of buffered hydrofluoric acid and alcohol (10:1) without stirring. In 275 minutes, only the single-crystal Si layer remained without etching, while the porous Si substrate was selectively etched with the single-crystal Si as a material for etching stopper and completely removed.

The etching rate of the non-porous Si single-crystal with the etching solution was extremely low, such as 100 angstroms or less even 275 minutes later, so that the selective ratio of the etching rate of the porous layer to that of the non-porous Si single-crystal was as large as 10⁵ or more. The etched amount in the non-porous layer (several tens angstroms) is a practically negligible decrease in membrane thickness. That is, the Si substrate of a thickness of 200 μ, rendered porous, was removed, and after the removal of the Si₃N₄ layer, a single-crystal Si layer of a thickness of 0.5 μm was formed on the substrate of the glass.

As a result of observation of the section under a transmission-type electron microscope, it was confirmed that no new crystal defect was introduced in the Si layer and that excellent crystallinity was maintained.

Examples 197 to 210

The same procedure as in Examples 42 to 55 was effected, replacing the etching solution in Examples 42 to 55 with that in Example 196. In any of the present Examples, consequently, a single-crystal Si layer was formed with extremely less crystal defect on insulating materials.

Example 211

A N-type Si layer of thickness of 1 μ was formed on the surface of a P-type Si layer of 200 μ in thickness, by ion implantation of proton. The implanted amount of H⁺ was 5 x 10¹⁵ ions/cm².

The substrate was anodized in 50 % HF solution. The current density then was 100 mA/cm². The porous structure formation rate then was 8.4 μm/min., and the N-type (100) Si substrate of a thickness of 200 μ was rendered porous in its entirety for 24 minutes. According to the present anodization as has been described abov . only th P-typ (100) Si substrat was rendered porous, but no change was observed in the N-type Si

layer.

Subs qu ntly, a second Si substrat n th surface of which was formed an oxidized lay r of 5000 angstroms was bonded t th surface f th N-type Si lay r. By heating in oxygen atmosph re at 800 °C for 0.5 hour, b th of the substrates were strongly bonded togeth r.

Then, th b nd d substrates were selectively etched with a mixed solution of buffered hydrofluoric acid (HF:4.46 %, NH₄F:36.2 %) and ethyl alcohol (10:1), without stirring. In 275 minutes, only th single-crystal Si layer r mained without tching, while the porous Si substrate was s lectiv ly etch d with the single-crystal Si as a material for etching stopper and then completely removed.

The etching rate of the non-porous Si single-crystal with the etching solution was extremely low, such as approximately slightly less than 40 angstroms even 275 minutes later, so that the selective ratio of the etching rate of the porous layer to that of the non-porous Si single-crystal was as large as 10^5 or more. The etched amount in the non-porous layer (several tens angstroms) is a practically negligible decrease in membrane thickness. That is, the Si substrate of a thickness of 200 μ, rendered porous, was removed, and a single-crystal Si layer of a thickness of 1.0 μm was formed on the SiO₂ layer.

As a result of observation of the section under a transmission-type electron microscope, it was confirmed that no new crystal defect was introduced in the Si layer and that excellent crystallinity was maintained.

Examples 212 to 226

The same procedure as in Examples 57 to 71 was effected, replacing the etching solution in Examples 57 to 71 with that in Example 196. In any of the present Examples, consequently, a single-crystal Si layer was formed with extremely less crystal defect on insulating materials.

Example 227

A P-type (100) single-crystal Si substrate of a thickness of 200 μ was anodized in 50% HF solution. The current density then was 100 mA/cm². The porous structure formation rate then was 8.4 μm/min., and the P-type (100) Si substrate of a thickness of 200 μ was rendered porous in its entirety for 24 minutes.

According to MBE (molecular beam epitaxy) method, an Si epitaxial layer of 0.5 μ was grown at a lower temperature on the P-type (100) porous Si substrate. The conditions for deposition are as follows;

temperature: 700 °C
pressure: 1 x 10⁻⁹ Torr
growth rate: 0.1 nm/sec.

Subsequently, a substrate of fused silica glass processed with optical polishing was bonded onto the surface of the epitaxial layer, and both of the substrates were strongly bonded together by heating at 800 °C for 0.5 hour in oxygen atmosphere.

According to plasma CVD method, Si₃N₄ was deposited to 0.1 μm, thereby coating the bonded two substrates. Thereafter, only the nitride membrane on the porous substrate was removed by reactive ion etching. Then, the bonded substrates were selectively etched in a mixed solution of buffered hydrofluoric acid and aqueous hydrogen peroxide solution (1:5) with stirring. In 190 minutes, only the single-crystal Si layer remained without etching, while the porous Si substrate was selectively etched with the single-crystal Si as a material for etching stopper, and completely removed.

The etching rate of the non-porous Si single-crystal with the etching solution was extremely low, such as 50 angstroms or less even 190 minutes later, so that the selective ratio of the etching rate of the porous layer to that of the non-porous Si single- crystal was as large as 10^5 or more. The etched amount in the non-porous layer (several tens angstroms) is a practically negligible decrease in membrane thickness. That is, the Si substrate of a thickness of 200 μ, rendered porous, was removed, and after the removal of the Si₃N₄ layer, a single-crystal Si layer of a thickness of 0.5 μm was formed on the substrate of the silica glass.

As a result of observation of the section under a transmission-type electron microscope, it was confirmed that no new crystal defect was introduced in the Si layer and that excellent crystallinity was maintained.

Examples 228 to 242

The same procedure as in Examples 42 to 56 was effected, replacing the etching solution in Examples 42 to 56 with that in Example 227. In any of the present Examples, consequently, a single-crystal Si layer was formed with extremely less crystal defect on insulating materials.

Example 243

A P-type (100) single-crystal Si substrat of a thickness of 200 μ was anodized in 50% HF solution. The current d nsity th n was 100 mA/cm². Th porous structure formation rate th n was about 8.4 μm/min., and the P-type (100) Si substrate of a thickness of 200 μ was rend red porous in its ntirety for 24 minutes.

According to MBE (mol cular b am epitaxy) method, an Si pitaxial layer of 0.5 μ was grown at a lower temperature on th P-typ (100) porous Si substrate. The conditions for d position ar as follows;

temperature: 700 °C
pressure: 1 x 10⁻⁹ Torr
growth rate: 0.1 nm/sec.

subsequently, the surface of the epitaxial layer was thermally oxidized in a depth of 50 nm. A substrate of fused silica glass processed with optical polishing was bonded onto the thermally oxidized membrane, and both of the substrates were strongly bonded together by heating at 800 °C for 0.5 hour in oxygen atmosphere.

According to low pressure CVD method, Si_3N_4 was deposited to 0.1 μm, thereby coating the bonded two substrates. Thereafter, only the nitride membrane on the porous substrate was removed by reactive ion etching.

Then, the bonded substrates were immersed in a mixed solution of buffered hydrofluoric acid and aqueous hydrogen peroxide solution (1:5), and stirred. In 190 minutes, only the single-crystal Si layer remained without etching, while the porous Si substrate was selectively etched with the single-crystal Si as a material for etching stopper and then completely removed.

The etching rate of the non-porous Si single-crystal with the etching solution was extremely low, such as 70 angstroms or less even 190 minutes later, so that the selective ratio of the etching rate of the porous layer to that of the non-porous Si single-crystal was as large as 10⁵ or more. The etched amount in the non-porous layer (several tens angstroms) is a practically negligible decrease in membrane thickness. That is, the Si substrate of a thickness of 200 μ, rendered porous, was removed, and after the removal of the Si_3N_4 layer, a single-crystal Si layer of a thickness of 0.5 μm was formed on the substrate of the silica glass.

As a result of observation of the section under a transmission-type electron microscope, it was confirmed that no new crystal defect was introduced in the Si layer and that excellent crystallinity was maintained.

Examples 244 to 257

The same procedure as in Examples 58 to 71 was effected, replacing the etching solution in Examples 58 to 71 with that in Example 243. In any of the present Examples, consequently, a single-crystal Si layer was formed with extremely less crystal defect on insulating materials.

Example 258

A P-type (100) single-crystal Si substrate of a thickness of 200 μ was anodized in 50 % HF solution. The current density then was 100 mA/cm². The porous structure formation rate then was 8.4 μm/min., and the P-type (100) Si substrate of a thickness of 200 μ was rendered porous in its entirety for 24 minutes.

According to MBE (molecular beam epitaxy) method, an Si epitaxial layer of 0.5 μ was grown at a lower temperature on the P-type (100) porous Si substrate. The conditions for deposition are as follows;

temperature: 700 °C
pressure: 1 x 10⁻⁹ Torr
growth rate: 0.1 nm/sec.

Subsequently, a substrate of fused silica glass processed with optical polishing was bonded onto the surface of the epitaxial layer, and both of the substrates were strongly bonded together by heating at 800 °C for 0.5 hour in oxygen atmosphere.

According to plasma CVD method, Si_3N_4 was deposited to 0.1 μm, thereby coating the bonded two substrates. Thereafter, only the nitride membrane on the porous substrate was removed by reactive ion etching.

Then, the bonded substrates were selectively etched in a mixed solution of buffered hydrofluoric acid, alcohol and aqueous hydrogen peroxide solution (10:6:50) without stirring. In 205 minutes, only the single-crystal Si layer remained without etching, while the porous Si substrate was selectively etched with the single-crystal Si as a material for etching stopper and then completely removed.

The etching rate of the non-porous Si single-crystal with the etching solution was extremely low, such as approximately slightly less than 40 angstroms even 205 minutes later, so that the selective ratio of the etching rate of the porous layer to that of the non-porous Si single-crystal was as large as 10⁵ or more. The etched amount in the non-porous layer (several tens angstroms) is a practically negligible decrease in membrane thickness. That is, the Si substrat of a thickness of 200 μ, rend red porous, was removed, and after the removal

of the Si₃N₄ layer, a single-crystal Si layer of a thickness of 0.5 μm was formed on th substrate of th silica glass.

As a result of observation of th section und r a transmission-type lectron microscope, it was confirm d that no new crystal def ct was introduced in the Si layer and that xcell nt crystallinity was maintained.

Exampl s 259 to 272

The same procedure as in Examples 42 to 55 was effected, replacing the etching solution in Examples 42 to 55 with that in Example 258. In any of the present Examples, consequently, a single-crystal Si layer was formed with extremely less crystal defect on insulating materials.

Example 273

A N-type Si layer of thickness of 1 μ was formed on the surface of a P-type (100) Si substrate of thickness of 200 μ, by ion implantation of proton. The implanted amount of H⁺ was 5×10^{15} ions/cm².

The substrate was anodized in 50 % HF solution. The current density then was 100 mA/cm². The porous structure formation rate then was 8.4 μm/min., and the P-type (100) Si substrate of a thickness of 200 μ was rendered porous in its entirety for 24 minutes. According to the present anodization as has been described above, only the P-type (100) Si substrate was rendered porous, but no change was observed in the N-type Si layer.

Subsequently, a second Si substrate on the surface of which was formed an oxidized layer of 5000 angstroms was bonded to the surface of the N-type Si layer. By heating in oxygen atmosphere at 800 °C for 0.5 hour, both of the substrates were strongly bonded together.

Then, the bonded substrates were selectively etched with a mixed solution of buffered hydrofluoric acid (HF:4.46 %, NH₄F:36.2%), ethyl alcohol and 30% aqueous hydrogen peroxide solution (10:6:50), without stirring. In 180 minutes, only the single-crystal Si layer remained without etching, while the porous Si substrate was selectively etched with the single-crystal Si as a material for etching stopper and then completely removed.

The etching rate of the non-porous Si single-crystal with the etching solution was extremely low, such as approximately slightly less than 40 angstroms even 180 minutes later, so that the selective ratio of the etching rate of the porous layer to that of the non-porous Si single-crystal was as large as 10⁵ or more. The etched amount in the non-porous layer (several tens angstroms) is a practically negligible decrease in membrane thickness. That is, the Si substrate of a thickness of 200 μ, rendered porous, was removed, and a single-crystal Si layer of a thickness of 1.0 μm was formed on the SiO₂ layer.

As a result of observation of the section under a transmission-type electron microscope, it was confirmed that no new crystal defect was introduced in the Si layer and that excellent crystallinity was maintained.

Examples 274 to 288

The same procedure as in Examples 57 to 71 was effected, replacing the etching solution in Examples 57 to 71 with that in Example 273. In any of the present Examples, consequently, a single-crystal Si layer was formed with extremely less crystal defect on insulating materials.

Claims

1. A chemical etching solution for porous Si comprising hydrofluoric acid as etchant.

2. A chemical etching solution for porous Si comprising a mixture of hydrofluoric acid and an alcohol as etchant.

3. A chemical etching solution for porous Si comprising a mixture of hydrofluoric acid and hydrogen peroxide as etchant.

4. A chemical etching solution for porous Si comprising a mixture of hydrofluoric acid, an alcohol and hydrogen peroxide as etchant.

5. A chemical etching solution for porous Si comprising buffered hydrofluoric acid as etchant.

6. A chemical etching solution for porous Si comprising a mixture of buffered hydrofluoric acid and an alcohol as tchant.

7. A chemical etching solution for porous Si comprising a mixture of buffered hydrofluoric acid and hydrog n p roxide as tchant.

8. A chemical etching solution for porous Si comprising a mixture of buffered hydrofluoric acid, an alcohol and hydrogen peroxide as etchant.

9. A chemical etching method for porous Si, which comprises using hydrofluoric acid as etchant.

10. A chemical etching method for porous Si, which comprises using a mixture of hydrofluoric acid and an alcohol as etchant.

11. A chemical etching method for porous Si, which comprises using a mixture of hydrofluoric acid and hydrogen peroxide as etchant.

12. A chemical etching method for porous Si, which comprises using a mixture of hydrofluoric acid, an alcohol and hydrogen peroxide as etchant.

13. A chemical etching method for porous Si, which comprises using buffered hydrofluoric acid as etchant.

14. A chemical etching method for porous Si, which comprises using a mixture of buffered hydrofluoric acid and an alcohol as etchant.

15. A chemical etching method for porous Si, which comprises using a mixture of buffered hydrofluoric acid and hydrogen peroxide as etchant.

16. A chemical etching method for porous Si, which comprises using a mixture of buffered hydrofluoric acid, an alcohol and hydrogen peroxide as etchant.

17. A method for preparing a semiconductor member, which comprises:
    forming a substrate having a non-porous silicon monocrystalline layer and a porous silicon layer;
    bonding another substrate having a surface made of an insulating material to the surface of said monocrystalline layer; and
    etching to remove said porous silicon layer by immersing in hydrofluoric acid.

18. A method for preparing a semiconductor member, which comprises:
    forming a substrate having a non-porous silicon monocrystalline layer and a porous silicon layer;
    bonding another substrate having a surface made of an insulating material to the surface of said monocrystalline layer; and
    etching to remove said porous silicon layer by immersing in a mixture of hydrofluoric acid and an alcohol.

19. A method for preparing a semiconductor member, which comprises:
    forming a substrate having a non-porous silicon monocrystalline layer and a porous silicon layer;
    bonding another substrate having a surface of an insulating material to the surface of said monocrystalline layer; and
    etching to remove said porous silicon layer by immersing in a mixture of hydrofluoric acid and hydrogen peroxide.

20. A method for preparing a semiconductor member, which comprises:
    forming a substrate having a non-porous silicon monocrystalline layer and a porous silicon layer;
    bonding another substrate having a surface made of an insulating material to the surface of said monocrystalline layer; and
    etching to remove said porous silicon layer by immersing in a mixture of hydrofluoric acid, an alcohol and hydrogen peroxide.

21. A method for preparing a semiconductor member, which comprises:
    forming a substrate having a non-porous silicon monocrystalline layer and a porous silicon layer;

bonding another substrate having a surface mad of an insulating material to the surface f said monocrystallin layer; and

etching to remov said porous silicon lay r by immersing in buff red hydrofluoric acid.

22. A method for preparing a semiconductor member, which comprises:

forming a substrate having a non-porous silicon monocrystallin lay r and a porous silicon lay r;

bonding another substrate having a surface made of an insulating material to the surface of said monocrystalline layer; and

etching to remove said porous silicon layer by immersing in a mixture of buffered hydrofluoric acid and an alcohol.

23. A method for preparing a semiconductor member, which comprises:

forming a substrate having a non-porous silicon monocrystalline layer and a porous silicon layer;

bonding another substrate having a surface made of an insulating material to the surface of said monocrystalline layer; and

etching to remove said porous silicon layer by immersing in a mixture of buffered hydrofluoric acid and hydrogen peroxide.

24. A method for preparing a semiconductor member, which comprises:

forming a substrate having a non-porous silicon monocrystalline layer and a porous silicon layer;

bonding another substrate having a surface made of an insulating material to the surface of said monocrystalline layer; and

etching to remove said porous silicon layer by immersing in a mixture of buffered hydrofluoric acid, an alcohol and hydrogen peroxide.

25. A method for preparing a semiconductor member, which comprises the steps of:

making a silicon substrate porous;

forming a non-porous silicon monocrystalline layer on said silicon substrate made porous;

bonding a light-transmissive glass substrate to the surface of said non-porous silicon monocrystalline layer; and

selectively etching porous silicon by chemically etching to remove porous silicon by immersing said silicon substrate made porous in hydrofluoric acid.

26. A method for preparing a semiconductor member, which comprises the steps of:

making a silicon substrate porous;

forming a non-porous silicon monocrystalline layer on the silicon substrate made porous;

bonding another silicon substrate having an insulating layer on the surface thereof to the surface of said non-porous silicon monocrystalline layer; and

selectively etching porous silicon by chemically etching to remove porous silicon by immersing said silicon substrate made porous in hydrofluoric acid.

27. A method for preparing a semiconductor member, which comprises the steps of:

making a silicon substrate porous;

forming a non-porous silicon monocrystalline layer on said silicon substrate made porous;

forming an oxide layer on the surface of said non-porous silicon monocrystalline layer;

bonding a light-transmissive substrate to the surface of said oxide layer; and

chemically etching to remove said silicon substrate made porous by immersing in hydrofluoric acid after coating the surfaces other than the surface of said silicon substrate made porous with a protecting material.

28. A method for preparing a semiconductor member, which comprises the steps of:

making a silicon substrate porous;

forming a non-porous silicon monocrystalline layer on said silicon substrate made porous;

forming an oxide layer on the surface of said non-porous silicon monocrystalline layer;

bonding another silicon substrate having an insulating material on the surface thereof to the surface of said oxide layer on said non-porous silicon monocrystalline layer; and

chemically etching to remove said silicon substrate made porous by immersing in hydrofluoric acid.

29. A m thod for preparing a semiconductor member, which comprises the steps of:

making a silicon substrate porous;

forming a non-porous silicon monocrystallin lay r n said silicon substrate mad porous;

bonding a light-transmissiv glass substrat t the surface of said non-porous silicon monocrystal-lin layer; and

s l ctively tching porous silicon by chemically etching to remove porous silicon by immersing said silicon substrate mad porous in a mixture of hydrofluoric acid and an alcohol.

30. A method for preparing a semiconductor member, which comprises the steps of:

making a silicon substrate porous;

forming a non-porous silicon monocrystalline layer on the silicon substrate made porous;

bonding another silicon substrate having an insulating layer on the surface thereof to the surface of said non-porous silicon monocrystalline layer; and

selectively etching porous silicon by chemically etching to remove porous silicon by immersing said silicon substrate made porous in a mixture of hydrofluoric acid and an alcohol.

31. A method for preparing a semiconductor member, which comprises the steps of:

making a silicon substrate porous;

forming a non-porous silicon monocrystalline layer on said silicon substrate made porous;

forming an oxide layer on the surface of said non-porous silicon monocrystalline layer;

bonding a light-transmissive substrate to the surface of said oxide layer; and

chemically etching to remove said silicon substrate made porous by immersing in a mixture of hyd-rofluoric acid and an alcohol after coating the surfaces other than the surface of said silicon substrate made porous with a protecting material.

32. A method for preparing a semiconductor member, which comprises the steps of:

making a silicon substrate porous;

forming a non-porous silicon monocrystalline layer on said silicon substrate made porous;

forming an oxide layer on the surface of said non-porous silicon monocrystalline layer;

bonding another silicon substrate having an insulating material on the surface thereof to the surface of said oxide layer on said non-porous silicon monocrystalline layer; and

chemically etching to remove said silicon substrate made porous by immersing in a mixture of hyd-rofluoric acid and an alcohol.

33. A method for preparing a semiconductor member, which comprises the steps of:

making a silicon substrate porous;

forming a non-porous silicon monocrystalline layer on said silicon substrate made porous;

bonding a light-transmissive glass substrate to the surface of said non-porous silicon monocrystal-line layer; and

selectively etching porous silicon by chemically etching to remove porous silicon by immersing said silicon substrate made porous in a mixture of hydrofluoric acid and hydrogen peroxide.

34. A method for preparing a semiconductor member, which comprises the steps of:

making a silicon substrate porous;

forming a non-porous silicon monocrystalline layer on the silicon substrate made porous;

bonding another silicon substrate having an insulating layer on the surface thereof to the surface of said non-porous silicon monocrystalline layer; and

selectively etching porous silicon by chemically etching to remove porous silicon by immersing said silicon substrate made porous in a mixture of hydrofluoric acid and hydrogen peroxide.

35. A method for preparing a semiconductor member, which comprises the steps of:

making a silicon substrate porous;

forming a non-porous silicon monocrystalline layer on said silicon substrate made porous;

forming an oxide layer on the surface of said non-porous silicon monocrystalline layer;

bonding a light-transmissive substrate to the surface of said oxide layer; and

chemically etching to remove said silicon substrate made porous by immersing in a mixture com-prising of hydrofluoric acid and hydrogen peroxide after coating the surfaces other than the surface of said silicon substrate made porous with a protecting material.

36. A m thod for preparing a s mic nductor m mber, which compris s th steps of:

making a silicon substrat porous;
forming a non-porous silicon monocrystallin lay r on said silicon substrate made porous;
forming an oxid layer on the surface of said non-porous silicon monocrystallin lay r,
bonding anoth r silicon substrate having an insulating material n th surface thereof to the surface of said oxid lay r on said non-porous silicon monocrystallin lay r, and
ch mically tching to remov said silicon substrate mad porous by imm rsing in a mixtur of hydrofluoric acid and hydrogen p roxide.

37. A method for preparing a semiconductor member, which comprises the steps of:
       making a silicon substrate porous;
       forming a non-porous silicon monocrystalline layer on said silicon substrate made porous;
       bonding a light-transmissive glass substrate to the surface of said non-porous silicon monocrystalline layer; and
       selectively etching porous silicon by chemically etching to remove porous silicon by immersing said silicon substrate made porous in a mixture of hydrofluoric acid, an alcohol and hydrogen peroxide.

38. A method for preparing a semiconductor member, which comprises the steps of:
       making a silicon substrate porous;
       forming a non-porous silicon monocrystalline layer on the silicon substrate made porous;
       bonding another silicon substrate having an insulating layer on the surface thereof to the surface of said non-porous silicon monocrystalline layer; and
       selectively etching porous silicon by chemically etching to remove porous silicon by immersing said silicon substrate made porous in a mixture of hydrofluoric acid, an alcohol and hydrogen peroxide.

39. A method for preparing a semiconductor member, which comprises the steps of:
       making a silicon substrate porous;
       forming a non-porous silicon monocrystalline layer on said silicon substrate made porous;
       forming an oxide layer on the surface of said non-porous silicon monocrystalline layer;
       bonding a light-transmissive substrate to the surface of said oxide layer; and
       chemically etching to remove said silicon substrate made porous by immersing in a mixture of hydrofluoric acid, an alcohol and hydrogen peroxide after coating the surfaces other than the surface of said silicon substrate made porous with a protecting material.

40. A method for preparing a semiconductor member, which comprises the steps of:
       making a silicon substrate porous;
       forming a non-porous silicon monocrystalline layer on said silicon substrate made porous;
       forming an oxide layer on the surface of said non-porous silicon monocrystalline layer;
       bonding another silicon substrate having an insulating material on the surface thereof to the surface of said oxide layer on said non-porous silicon monocrystalline layer; and
       chemically etching to remove said silicon substrate made porous by immersing in a mixture of hydrofluoric acid, an alcohol and hydrogen peroxide.

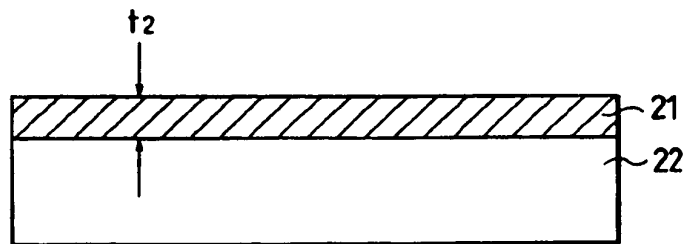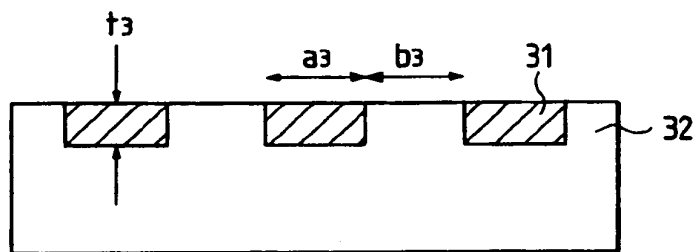41. A method for preparing a semiconductor member, which comprises the steps of:
       making a silicon substrate porous;
       forming a non-porous silicon monocrystalline layer on said silicon substrate made porous;
       bonding a light-transmissive glass substrate to the surface of said non-porous silicon monocrystalline layer; and
       selectively etching porous silicon by chemically etching to remove porous silicon by immersing said silicon substrate made porous in buffered hydrofluoric acid.

42. A method for preparing a semiconductor member, which comprises the steps of:
       making a silicon substrate porous;
       forming a non-porous silicon monocrystalline layer on the silicon substrate made porous;
       bonding another silicon substrate having an insulating layer on the surface thereof to the surface of said non-porous silicon monocrystalline layer; and
       selectively etching porous silicon by chemically etching to remove porous silicon by immersing said silicon substrate made porous in buffered hydrofluoric acid.

43. A method for pr paring a semiconductor member, which compris s th steps of:

making a silicon substrate porous;

forming a non-porous silic n monocrystalline lay r on said silicon substrate mad porous;

forming an oxid layer n the surface of said non-porous silicon monocrystallin lay r,

bonding a light-transmissiv substrate to the surface of said oxide layer, and

chemically etching to remove said silicon substrat made porous by immersing in buffered hydrofluoric acid after coating the surfaces ther than the surface of said silicon substrate mad porous with a protecting material.

44. A method for preparing a semiconductor member, which comprises the steps of:

making a silicon substrate porous;

forming a non-porous silicon monocrystalline layer on said silicon substrate made porous;

forming an oxide layer on the surface of said non-porous silicon monocrystalline layer,

bonding another silicon substrate having an insulating material on the surface thereof to the surface of said oxide layer on said non-porous silicon monocrystalline layer; and

chemically etching to remove said silicon substrate made porous by immersing in buffered hydrofluoric acid.

45. A method for preparing a semiconductor member, which comprises the steps of:

making a silicon substrate porous;

forming a non-porous silicon monocrystalline layer on said silicon substrate made porous;

bonding a light-transmissive glass substrate to the surface of said non-porous silicon monocrystalline layer; and

selectively etching porous silicon by chemically etching to remove porous silicon by immersing said silicon substrate made porous in a mixture of buffered hydrofluoric acid and an alcohol.

46. A method for preparing a semiconductor member, which comprises the steps of:

making a silicon substrate porous;

forming a non-porous silicon monocrystalline layer on the silicon substrate made porous;

bonding another silicon substrate having an insulating layer on the surface thereof to the surface of said non-porous silicon monocrystalline layer; and

selectively etching porous silicon by chemically etching to remove porous silicon by immersing said silicon substrate made porous in a mixture of buffered hydrofluoric acid and an alcohol.

47. A method for preparing a semiconductor member, which comprises the steps of:

making a silicon substrate porous;

forming a non-porous silicon monocrystalline layer on said silicon substrate made porous;

forming an oxide layer on the surface of said non-porous silicon monocrystalline layer,

bonding a light-transmissive substrate to the surface of said oxide layer, and

chemically etching to remove said silicon substrate made porous by immersing in a mixture of buffered hydrofluoric acid and an alcohol after coating the surfaces other than the surface of said silicon substrate made porous with a protecting material.

48. A method for preparing a semiconductor member, which comprises the steps of:

making a silicon substrate porous;

forming a non-porous silicon monocrystalline layer on said silicon substrate made porous;

forming an oxide layer on the surface of said non-porous silicon monocrystalline layer,

bonding another silicon substrate having an insulating material on the surface thereof to the surface of said oxide layer on said non-porous silicon monocrystalline layer; and

chemically etching to remove said silicon substrate made porous by immersing in a mixture of buffered hydrofluoric acid and an alcohol.

49. A method for preparing a semiconductor member, which comprises the steps of:

making a silicon substrate porous;

forming a non-porous silicon monocrystalline layer on said silicon substrate made porous;

bonding a light-transmissive glass substrate to the surface of said non-porous silicon monocrystalline layer; and

selectively etching porous silicon by chemically etching to remove porous silicon by immersing said silicon substrate made porous in a mixture of buffered hydrofluoric acid and hydrogen peroxide.

50. A method for preparing a semiconductor member, which comprises the teps of:
    making a silicon substrate porous;
    forming a non-porous silicon monocrystalline lay r on th ilicon substrate mad porous;
    bonding another silicon substrate having an insulating lay r on the surface thereof to the surface
    of said non-porous silicon monocrystalline lay r; and
    selectively etching porous silicon by chemically etching to remov porous silicon by immersing said
    silicon substrate made porous in a mixture of buffered hydrofluoric acid and hydrogen peroxide.

51. A method for preparing a semiconductor member, which comprises the steps of:
    making a silicon substrate porous;
    forming a non-porous silicon monocrystalline layer on said silicon substrate made porous;
    forming an oxide layer on the surface of said non-porous silicon monocrystalline layer;
    bonding a light-transmissive substrate to the surface of said oxide layer; and
    chemically etching to remove said silicon substrate made porous by immersing in a mixture com-
    prising buffered hydrofluoric acid and hydrogen peroxide after coating the surfaces other than the surface
    of said silicon substrate made porous with a protecting material.

52. A method for preparing a semiconductor member, which comprises the steps of:
    making a silicon substrate porous;
    forming a non-porous silicon monocrystalline layer on said silicon substrate made porous;
    forming an oxide layer on the surface of said non-porous silicon monocrystalline layer;
    bonding another silicon substrate having an insulating material on the surface thereof to the surface
    of said oxide layer on said non-porous silicon monocrystalline layer; and
    chemically etching to remove said silicon substrate made porous by immersing in a mixture of buf-
    fered hydrofluoric acid and hydrogen peroxide.

53. A method for preparing a semiconductor member, which comprises the steps of:
    making a silicon substrate porous;
    forming a non-porous silicon monocrystalline layer on said silicon substrate made porous;
    bonding a light-transmissive glass substrate to the surface of said non-porous silicon monocrystal-
    line layer; and
    selectively etching porous silicon by chemically etching to remove porous silicon by immersing said
    silicon substrate made porous in a mixture of buffered hydrofluoric acid, an alcohol and hydrogen peroxide.

54. A method for preparing a semiconductor member, which comprises the steps of:
    making a silicon substrate porous;
    forming a non-porous silicon monocrystalline layer on the silicon substrate made porous;
    bonding another silicon substrate having an insulating layer on the surface thereof to the surface
    of said non-porous silicon monocrystalline layer; and
    selectively etching porous silicon by chemically etching to remove porous silicon by immersing said
    silicon substrate made porous in a mixture of buffered hydrofluoric acid, an alcohol and hydrogen peroxide.

55. A method for preparing a semiconductor member, which comprises the steps of:
    making a silicon substrate porous;
    forming a non-porous silicon monocrystalline layer on said silicon substrate made porous;
    forming an oxide layer on the surface of said non-porous silicon monocrystalline layer;
    bonding a light-transmissive substrate to the surface of said oxide layer; and
    chemically etching to remove said silicon substrate made porous by immersing in a mixture of buf-
    fered hydrofluoric acid, an alcohol and hydrogen peroxide after coating the surfaces other than the surface
    of said silicon substrate made porous with a protecting material.

56. A method for preparing a semiconductor member, which comprises the steps of:
    making a silicon substrate porous;
    forming a non-porous silicon monocrystalline layer on said silicon substrate made porous;
    forming an oxide layer on the surface of said non-porous silicon monocrystalline layer;
    bonding another silicon substrate having an insulating material on the surface thereof to the surface
    of said oxide layer on said non-porous silicon monocrystalline layer; and
    chemically etching to remove said silicon substrate made porous by immersing in a mixture com-
    prising buffered hydrofluoric acid, an alcohol and hydrogen peroxide.

FIG. 1A

t_2
21
22

FIG. 1B

22

FIG. 2A
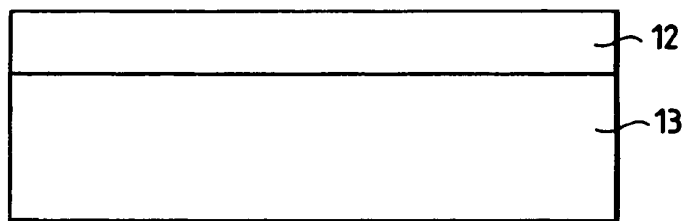
t_3
a_3 b_3 31
32

FIG. 2B

32

FIG. 3A

U4

41

42

FIG. 3B

t4

43
41
42

FIG. 3C

41

42

FIG. 4A

FIG. 4B

FIG. 4C

FIG. 5A

t_6

61

62

FIG. 5B

a_6 b_6

63

61

62

FIG. 5C

63

61

62

FIG. 5D

61

62

FIG. 6A

FIG. 6B

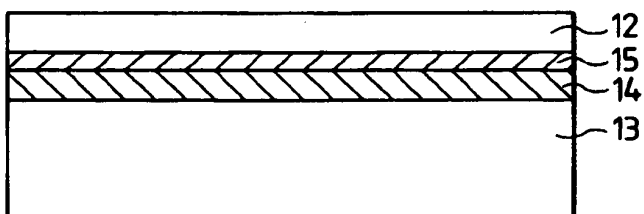# FIG. 6C

FIG. 6D

FIG. 6E
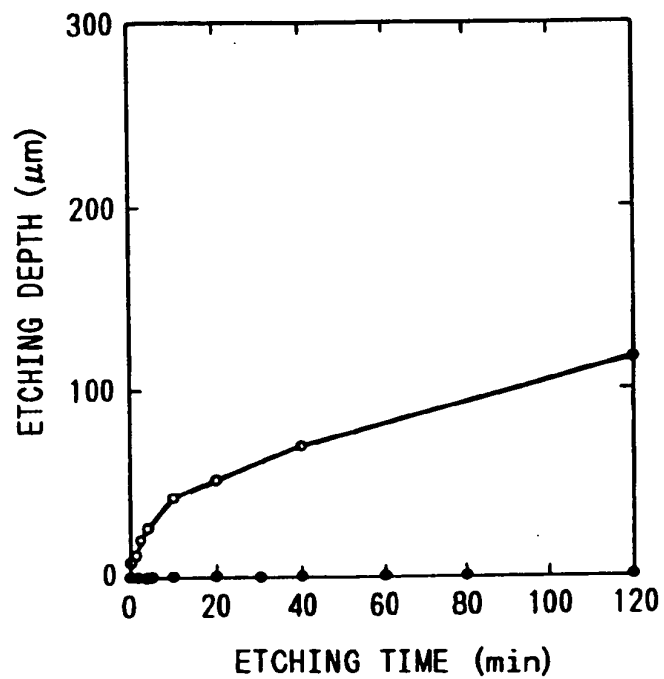
FIG. 6F
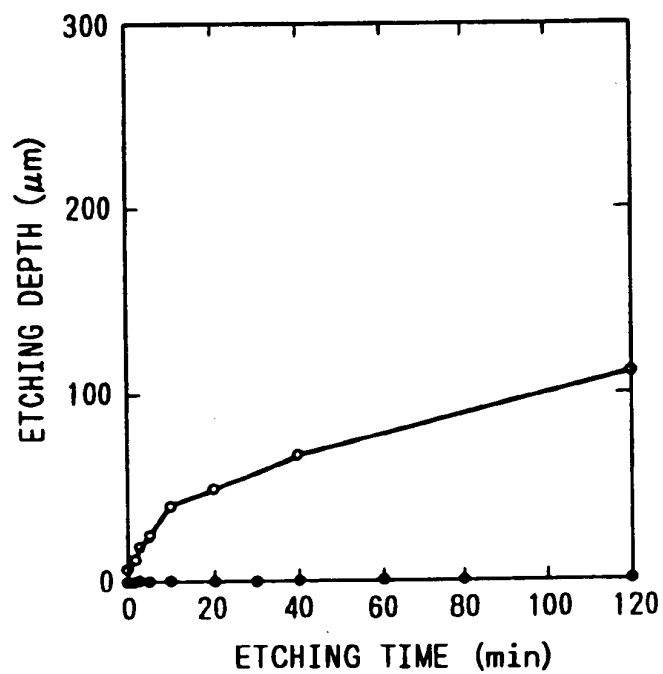
FIG. 6G
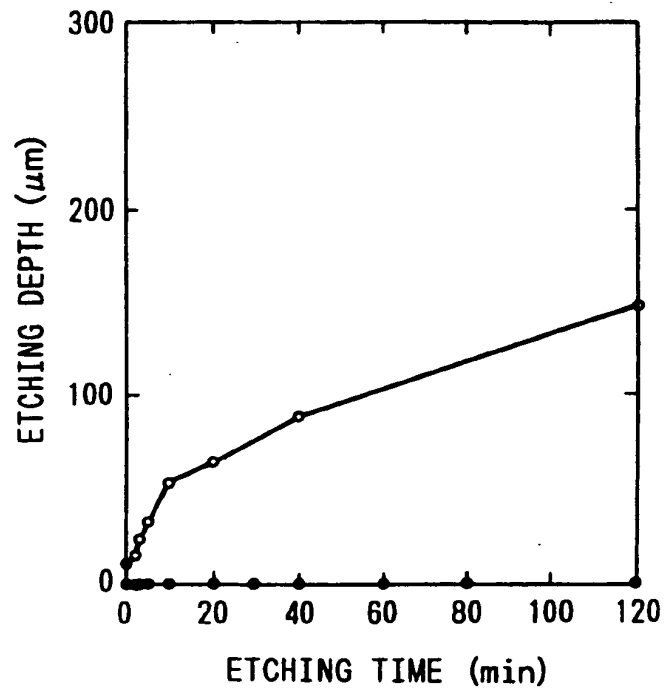
FIG. 6H
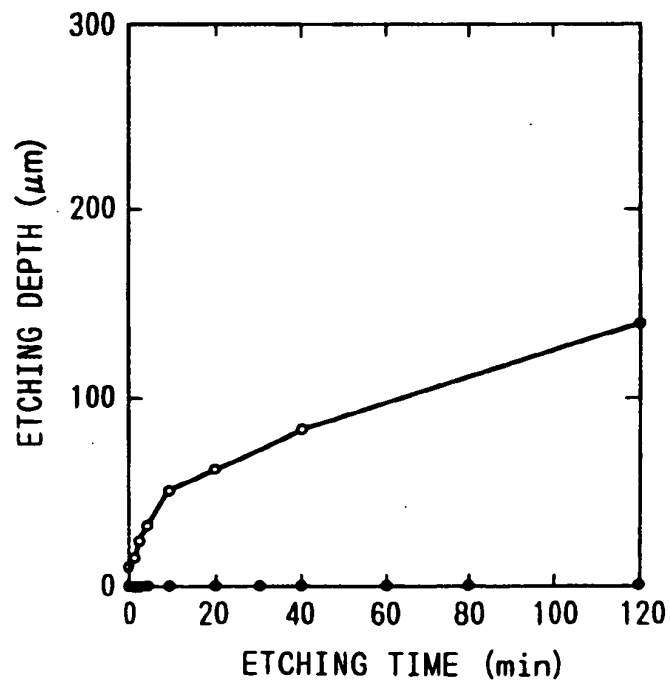
FIG. 7A
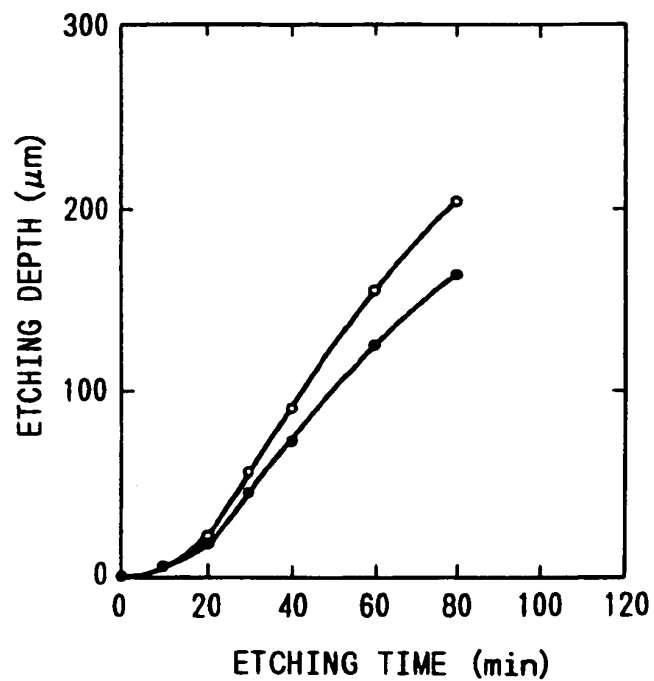
FIG. 7B
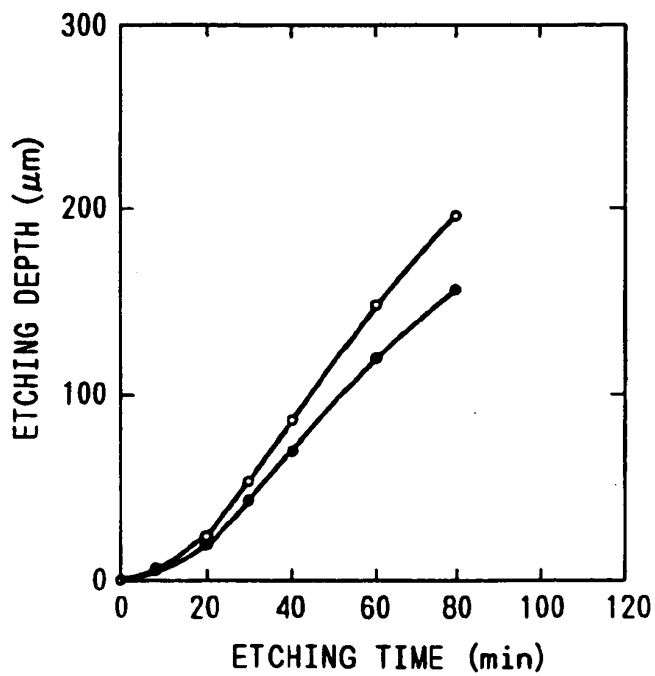
FIG. 7C

FIG. 7D

FIG. 7E

FIG. 7F

FIG. 7G

FIG. 7H

FIG. 8A

FIG. 8B

FIG. 8C

FIG. 9A

FIG. 9B

FIG. 9C

FIG. 9D

FIG. 10A

12

11

FIG. 10B

11

12

14

13

FIG. 10C

12

14

13

FIG. 11A

22
21

FIG. 11B

22
23

FIG. 11C

23
22
25
24

FIG. 11D

22
25
24

FIG. 12A

FIG. 12B

FIG. 12C

FIG. 13A

FIG. 13B

FIG. 13C

FIG. 14A

FIG. 14B

FIG. 14C

FIG. 14D

EUROPEAN PATENT APPLICATION

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EP 0 499 488 A3

(54) Etching solution for etching porous silicon, etching method using the etching solution and method of preparing semiconductor member using the etching solution.

(57) A method for preparing a semiconductor member comprises :
forming a substrate having a non-porous silicon monocrystalline layer and a porous silicon layer ;
bonding another substrate having a surface made of an insulating material to the surface of the monocrystalline layer ; and
etching to remove the porous silicon layer by immersing in an etching solution.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 1252

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	APPLIED PHYSICS LETTERS., vol.57, no.10, 3 September 1990, NEW YORK US pages 1046 - 1048 L.T. CANHAM 'SILCON QUANTUM WIRE ARRAY FABRICATION BY ELECTROCHEMICAL AND CHEMICAL DISSOLUTION OF WAFERS.' * page 1047, left column, paragraph 4 - page 1048, left column, paragraph 2; figure 3 *	1,9	H01L21/306 H01L21/20 H01L21/76
P,X	WO-A-91 09420 (SECR. OF STATE FOR DEF. IN HER BR. MAJEST. GOVERN. U.K GB & N. IR) * claims 1,5,7; figures 6,7 *	1,2,9,10	
A	US-A-3 962 052 (IBM) * column 3, line 13 - line 36; claim 1 *	1,17-56	
A	FR-A-2 374 396 (IBM) * claims 1,4 *	1	
X	* claims 6-12 *	3,5,7, 11,13,15	TECHNICAL FIELDS SEARCHED (Int.Cl.5) H01L
A	IBM TECHNICAL DISCLOSURE BULLETIN., vol.14, no.11, April 1972, NEW YORK US G.H. SCHWUTTKE ET AL. 'ETCHING OF VERTICAL WALLED PATTERNS IN (100) SILICON.'		
A	JOURNAL OF THE ELECTROCHEMICAL SOCIETY, vol.131, no.3, March 1984, MANCHESTER, NEW HAMPSHIRE US pages 672 - 674 L. LIOU ET AL. 'AMORPHOUS SILICON PRODUCED BY ION IMPLANTATION. ETCHING RATE IN HF SOLUTIONS AND EFFECT OF ANNEALING.'		

-/--

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23 December 1994	Vancraeynest, F

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
A	JOURNAL OF THE ELECTROCHEMICAL SOCIETY, vol.114, no.4, April 1967, MANCHESTER, NEW HAMPSHIRE US page 114 S.M. HU ET AL. 'OBSERVATION OF ETCHING OF N-TYPE SILICON IN AQUEOUS HF SOLUTIONS' ---		
P,A	EP-A-0 469 630 (CANON) * claims 1-125 * ---	17-56	
A	EP-A-0 209 173 (PHILIPS N.V.) * claims 1-8,10,22,23 * ---	17-56	
A	EXTENDED ABSTRACTS OF THE 20TH (1988 INTERNATIONAL) CONFERENCE ON SOLID-STATE DEVICES AND MATERIALS 1988, 1988, TOKYO pages 33 - 36 A. NAKAGAWA ET AL. '500V LATERAL DOUBLE GATE BIPOLAR-MODE MOSFET(DGIGBT) DIELECTRICALLY ISOLATED BY SILICON WAFER DIRECT-BONDING (DISDB).' * figure 1 * ---	17-56	TECHNICAL FIELDS SEARCHED (Int.Cl.5)
A	JOURNAL OF THE ELECTROCHEMICAL SOCIETY, vol.135, no.8, August 1988, MANCHESTER, NEW HAMPSHIRE US pages 2105 - 2107 X.- Z. TU 'FABRICATION OF SILICOON MICROSTRUCTURES BASED ON SELECTIVE FORMATION AND ETCHING OF POROUS SILICON' * page 2106, left column, paragraph 3 - right column, paragraph 8; figure 1 * ---	2-16	

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23 December 1994	Vancraeynest, F

CATEGORY OF CITED DOCUMENTS

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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 1252

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
A	CHEM. PRUM., vol.27, no.12, 1977, PRAQUE pages 602 - 606 SEBEK SVATOPLUK 'CHEMICAL ETCHING OF THE SURFACE OF SILICON SINGLE CRYSTALS' & CHEMICAL ABSTRACTS, vol.88, no.20, 15 May 1978, OHIO page 595 'ABSTRACT NO 145042' ---	1,3,11	
A	PATENT ABSTRACTS OF JAPAN vol. 14, no. 580 (E-1017) 25 December 1992 & JP-A-02 252 265 (SONY) 11 October 1990 * abstract * -----	1-56	

TECHNICAL FIELDS
SEARCHED   (Int.Cl.5)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23 December 1994	Vancraeynest, F

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L : document cited for other reasons

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EP 98 30 1252

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

☐ All claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for all claims.

☐ Only part of the claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid.

namely claims:

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions,
namely:

See Sheet B.

☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid.

namely claims:

☐ None of the further search fees has been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims.

namely claims:

European Patent
Office

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims 1, 9: HF etchant for porous Si, and method for etching porous Si using HF etchant

2. Claims 2-8, 10-16: Mixture of HF as etchant for porous Si, and method of etching using such a mixture of HF for porous Si

3. Claims 17-56: Formation of an SOI structure